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1929-1930.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. Alexander Duckham is on a visit to Trinidad.

Mr. J. E. Duckham is on a tour in South Africa.

Mr. J. O. Guthrie is home from Burma.

Mr. W. R. S. Henderson has left for Canada.

Mr. George Johnston is home from Venezuela.

Commander H. V. Lavington has left Trinidad and is in Ecuador.

Mr. F. M. Marshall has left for Persia.

Ing. J. Martynik is in Germany.

Mr. R. H. Mitchell has left for Venezuela.

Mr. C. F. C. Moore is in India.

Mr. P. E. T. O'Connor is leaving for Rumania.

Mr. R. M. S. Owen is in Canada.

Mr. R. G. B. Pringle has left for Iraq.

Mr. D. P. Rees has returned to Burma.

Mr. F. Sager is in Italy.

Mr. E. C. Scott has returned from Trinidad.

Mr. R. G. Stuttle has returned to Persia.

The Secretary will be glad to receive information as to the whereabouts of the following members :—C. A. BAUDUIN, J. C. FORTUNE, C. W. FULCHER, W. J. HARRIS, L. B. HOLLOWAY, W. JOHNSTON, A. F. C. PARKER, L. R. PHILLIPS and F. E. G. WATSON.

The Institution is greatly indebted to Mrs. W. H. Dalton for the presentation of the Bibliography of Petroleum Literature compiled by the late Mr. W. H. Dalton. This Bibliography, which comprises over 30,000 references to published works on petroleum and allied substances, is in slip form and is now in the Library of the Institution. It may be consulted on application to the Librarian.

NOMINATIONS FOR MEMBERSHIP OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The following have been nominated for membership of the Institution of Petroleum Technologists and their Application Forms may be seen at the Offices of the Institution :—

As Members.—Donald Charles Broome, William John Burchett, Douglas Harold Jackson, Arthur Whittaker Richardson.

Transfer to Member.—Henry Frederick Moon.

As Associate Members.—Henry Norman Bassett, John Howard-Glossop Goodfellow.

Transfer to Associate Member.—David Glynn Jones.

As Students.—Reginald Charles Rogers, Herbert William Harry Wilkinson.

UNIVERSITY OF MICHIGAN.

The announcement of the Courses in Chemical Engineering for 1930 is of importance to petroleum technologists as the various courses include a number of direct interest in petroleum technology.

The Department of Engineering Research has important contacts with the chemical industry and several industrial fellowships will be available for graduate students, for which application should be made by April 1.

Copies of the Bulletin giving particulars of the Courses may be obtained on application to the Chemical Engineering Department, University of Michigan, Ann Arbor, Michigan, U.S.A. This Bulletin also contains a bibliography of research papers and those of Prof. C. G. Brown and Prof. E. H. Leslie should prove of interest to petroleum technologists.

A new house journal made its appearance in January, 1930, under the title of Leyland Rubber Relay, being published by the Leyland and Birmingham Rubber Co., Ltd. The objects of this journal, apart from dealing with matters of personal interest to members of the firm's staff, is to give information as to the activities of the Company, how its products are made, and how its factories are progressing. At present it will be published every two months.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND TWENTY-FOURTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, January 14th, 1930, the Chair being occupied by the President, Dr. A. E. Dunstan.

The Secretary read the following lists of newly-elected members and persons nominated for membership :—

The following gentlemen have been elected :—

As Members.—Thomas Michael Hartigan, Percy Norman Hulme, Hugh McCallum MacIntyre, Malcolm Smythe Mainland, Jules Rimbaut, Casimir Zuber, Stanislaw Zuber.

As Associate Members.—Christopher Wilfred Percy Edmund Green, Alexander Thomas Spence Simpson.

As Transfer to Associate Member.—Horace Vivian Steadman.

As Students.—Michael Ross Burnett, Duncan Alexander Cox Dewdney, Reza Khan Fallah, Roy Bruce Finnis, Alan Lancelot Greig, Norman George Gullick, Edward James Stanley Hewitt, George Douglas Hobson, Robert Elliott James, Charles Stirling Lee, Abbas Parkhideh, Paul Pewsner, Abol Hassan Khan Radjy, Alfred Siff, Richard Colin Simmonds, Adrian Jasper Ernest Swann, Theodorus Willem Te Nuyl, Edward Ernest Thorneloe.

At the Council Meeting, held on December 10th, 1929, the following were nominated :—

As Members.—Bert Charles Frichot, Philip Morley Griffiths, Walter James Perelis, Charles William Burt Shorto.

As Transfer to Member.—Gwyn Elias, Henry Stuart Tegner.

As Associate Members.—William Parkinson Hirst, Stanley Lashmore Roberts, George Vernon Tullett, John Campbell Wright Robb.

As Students.—Henry Cecil Hastings Darley, Michael Everitt Kelly, James Francis Alexander Stark, Thomas Charles Gordon Thorpe.

As Associate.—Reginald Frank Alfred Baldwin.

At the Council Meeting, held on January 14th, 1930, the following were nominated :—

As Members.—Donald Charles Broome, William John Burchett, Douglas Harold Jackson, Arthur Whittaker Richardson.

As Transfer to Member.—Henry Frederick Moon.

As Associate Members.—Henry Norman Bassett, John Howard-Glossop Goodfellow.

As Transfer to Associate Member.—David Glynn Jones.

As Students.—Reginald Charles Rogers, Herbert William Harry Wilkinson.

The President said it was a great pleasure to him to welcome once more Mr. A. A. Ashworth, and he would ask him to read his paper.

Efficiency in the Distillation of Light Oils from Crude Oil.

By A. A. Ashworth, M.A., A.M.Inst.C.E. (Member).

In considering the question of the efficiency of a refinery it is too often assumed that a close approximation to the maximum value obtainable from the crude is being realised, and that only by reducing working costs can the efficiency and, therefore, the profits be appreciably increased.

Some time ago the writer was asked the specific question: "Is this refinery getting the maximum value out of the crude oil run and, if not, what proportion of the maximum value is it getting?"

The problem thus stated is not concerned with working costs nor with what products should be made, but deals purely with the question of value obtained from the crude oil in the ordinary course of running.

It is evident that the first step towards answering this question was to devise some means whereby the maximum value could be ascertained by laboratory analysis. The too usual method of making a laboratory distillation, cutting the fractions at certain arbitrary temperatures and assuming that these fractions represented the maximum content of the corresponding products, benzine, kerosine, etc., was obviously too empiric to be of any use.

In view of the overlapping of the distillation ranges as given by the specifications to which the several light products had to conform, a method of laboratory analysis by means of which

the maximum value could be calculated with a fair amount of exactitude was not immediately apparent. The following are the specifications of the standard products regularly made by the refinery which, it may be mentioned, was situated in Rumania :

Light benzine.—60 per cent. by volume to distil below 100° C. Final boiling point not above 150° C. Specific gravity not above 0·728/15° C. 98 per cent. to be recovered in the Engler distillation.

Heavy benzine.—Initial boiling point not above 100° C. Final boiling point not above 175° C. Specific gravity not above 0·765/15° C.

White spirit No. 1.—Initial boiling point not above 130° C. Not more than 2 per cent. to distil below 140° C. Final boiling point not above 200° C. Specific gravity not above 0·788/15° C. Flash-point above 28° C.

Kerosine.—Maximum specific gravity 0·825/15° C. 94 per cent. to distil over below 280° C. Flash-point above 27° C.

Gas oil.—Minimum specific gravity 0·845/15° C. 92 per cent. to distil over below 350° C. Flash-point above 65° C.

It may be noted that the overlap between light benzine and heavy benzine in the above specification is 50° C. and that between heavy benzine and white spirit 35° to 45° C. In view of this overlap, a simple distillation to produce the distillates directly from the crude oil could not give definite proportions between the amounts of the several distillates obtainable.

A more critical examination of the specifications, however, showed that certain definite " cut points " were indicated. These were as follows :—

Initial boiling point to 100° C.—This cut is a part of the light benzine and is not included in any of the other products.

100° C. *to* 130/140° C.—This cut forms part of the light benzine and also of the heavy benzine, but is not included in any of the other distillates.

130°/140° C. *to* 150° C.—This cut forms part of the light benzine, the heavy benzine and the white spirit.

150° C. *to* 175° C.—This cut forms part of the heavy benzine and the white spirit.

175° C. *to* 200° C.—This cut forms part of the white spirit. It may also enter into the composition of the kerosine but not necessarily according to the specification.

200° C. *to* 280° C.—This cut forms part of the kerosine. It may not be possible, and generally in the case of Rumanian crudes it is impossible, to include the whole of this cut on account of the limit of 0·825 for the specific gravity.

280° C. *to* 300° C.—This cut will form part of the gas oil. At 300° C. vapour temperature the distillation for light oils will terminate, as above this temperature cracking will almost certainly take place, spoiling the flash-point of the gas oil.

A laboratory distillation of the crude oil with fairly complete separation of the fractions into the above cuts seemed to offer a solution of the problem of obtaining the maximum value of light products from a given sample of crude oil.

On further examination, some modifications of the suggestion to distil the crude oil into the above temperature cuts seemed advisable.

Cut point at 100° C.—Part of the fraction from 100° C. to 130/140° C. is required to form part of the heavy benzine when blended with the higher cuts. Such blending will cause a slight raising of the initial point of the blend when tested by the Engler distillation. For this reason it is better to reduce the 100° C. temperature to 97° C.

Cut point at 130°/140° C.—This cut point might be made anywhere between 130° and 140°. Actual experience showed that 136° was a useful temperature for the following reasons. It is close enough to 140° to ensure the fulfilment of the initial distillation clause in the white spirit specification to the effect that not more than 2 per cent. should distil over below 140°, and also it provided more than sufficient of the cut from 100° to 136° to blend with the first cut to make all the light benzine possible and leave enough of the second cut to make the heavy benzine required. It would only be in the case of exceptionally light crude oils such as are not yet produced in Rumania in any large quantity that more of this second cut would be required for the light benzine.

Cut point at 150° C.—In view of the above, this cut point can be omitted. Although the final boiling point of the light benzine is 150° C., for maximum yield it is not advisable to go so high. This is apparent when it is considered that light benzine is a blend of the first cut, that up to 97° C. with sufficient of the second cut to give a volatility of 60 per cent. over at 100° C. With a given amount of the first cut, more of this second cut can be incorporated and still retain the desired volatility the lighter this second cut is. In other words, with all except the very light crude oils, the control point in the light benzine specification is the volatility and not the end point.

The final selection of the cut points was as follows:—

Cut (1).—Initial boiling point of crude to 97° C.

Cut (2).—97° C. to 136° C.

Cut (3).—136° C. to 175° C.

Cut (4).—175° C. to 200° C.

Cut (5).—200° C. to 280° C. or, in the case of most crude oils, to the point necessary to give the limiting specific gravity of 0·825 for the kerosine.

Cut (6).—From the end of Cut (5) to 300° C.

The apparatus used for this laboratory analysis comprises a 1500 c.c. short necked flask fitted with a column 1½ in. dia. containing 15 in. of column filling consisting of Raschig or Lessing rings or jack chain. The flask is enclosed in an asbestos millboard box up to the level of the cork. This is in order to jacket the flask with the hot products of combustion from the gas flame and prevent condensation in the flask itself. The column is provided with removable sections of insulation, so that more or less condensation can be allowed in the column to provide reflux. With the full amount of insulation on the column, reflux is almost totally prevented.

The degree of fractionation obtainable with this column is sufficient for the purpose for which it was designed in that the temperatures at which the various cuts are made check with the temperatures found in making the subsequent Engler distillations of the final products; for instance, a white spirit made with Cut (4) will have a final boiling point of 200° C. when tested by an Engler distillation.

In order to explain the making of the standard products specified above, it is necessary to go into rather full detail of the system of analysis as made in the laboratory.

1000 gms. of the crude oil are charged into the flask and distillation commenced without any insulation on the column, so as to give the maximum amount of reflux. Distillation is carried out at a fair rate until nearing the first cut point of 97° C. When within about five degrees of the cut point, distillation is slowed down to about two drops a second until the temperature is reached, when the receiver is changed. The weight, volume and specific gravity of the cut is measured and noted while Cut (2) is distilling.

In the case of crude oil containing moisture, the 97° cut cannot be made in this first distillation owing to the error introduced by the partial pressure of the water vapour. In such cases it is necessary to continue to the end of Cut (2) at 136° C. and, after settling out the water from the combined cuts, refractionate these in a similar apparatus to obtain the proportions, weights and specific gravities of Cuts (1) and (2). The presence of water vapour is always apparent by the occurrence of condensed water at the top of the column.

When Cut (2) is distilled, so much of it is taken and blended with Cut (1) as is necessary to make a light benzine which will distil

60 per cent. up to 100° C. in an Engler flask. The proportions of Cuts (1) and (2) will vary somewhat with different crude oils and the exact amount must be found by experiment. Generally about 52 per cent. of (1) with 48 per cent. of (2) are required. If this does not give an exact volatility of 60 per cent., the difference will be small and the exact percentages estimated without making a second trial.

The remainder of Cut (2) must be blended with sufficient of Cut (3), that up to 175° C., to make a heavy benzine of sp. gr. 0·765. This is a matter of arithmetical calculation once the specific gravities of Cuts (2) and (3) are known.

The remainder of Cut (3) must be blended with sufficient of Cut (4) to give a white spirit of sp. gr. 0·788. This is again a matter of arithmetic, and the calculation is made while Cut (5) is in course of distillation.

The balance of Cut (4) which is not taken up by the white spirit is poured into the receiver, into which Cut (5) is being distilled. A hydrometer and wire stirrer are also inserted, and distillation of Cut (5) is continued until the specific gravity of the product in the receiver reaches 0·825, that specified or kerosine.

During the distillation of Cut (5), insulation has to be placed on the column, otherwise column condensation and reflux become too heavy. When Cut (5) is complete and the final Cut (6) is being distilled for gas oil, the column should be insulated to the top as no fractionation is desirable.

In Rumania the white spirit and the kerosine are chemically refined. Depending on the crude oil, this treatment will cause certain inevitable refining losses, generally about 0·8 per cent. for white spirit and 1·0 per cent. for kerosine. As these losses are inevitable, they are deducted from the percentages of the white spirit and kerosine distillates in estimating the maximum quantities of these standard products obtainable from the crude oil run by the refinery.

A similar deduction is made from the total to allow for the condensation loss as found in making this laboratory analysis. Assuming that the laboratory analysis is made with every care taken to avoid condensation loss, a certain amount of such loss is inevitable and is due to dissolved gas in the crude oil. Such loss as is found in the laboratory is considered to be inherent in the crude oil and not due to refinery inefficiency.

The blending of the cuts in this system of analysis gives the control chemist the power of varying the proportions of the final percentages of standard products to some extent in accordance with the F.O.B. Refinery prices for these products during the month. For instance, during a part of the writer's stay in Rumania, the

price of white spirit was higher than that of heavy benzine. During this period Cut (3) was not blended with Cut (2) to form heavy benzine, but was all used in making white spirit by blending with Cut (4). This procedure naturally reduced the amount of kerosine, but on the whole gave a higher total value for the products. It also produced much too good a heavy benzine, but nevertheless was of advantage in obtaining value from the crude oil.

The main principle in this system of analysis is to substitute for the usual empiric system a system based on the actual temperatures indicated in the specifications whereby a series of definite cuts is obtained, and then, mainly by arithmetical computation, to combine these cuts so as to give the maximum value of products obtainable from the crude oil. It may be pointed out that, by this laboratory analysis, the actual products are obtained and not merely estimated.

Having evolved a system of laboratory analysis which enabled a fairly close approximation to maximum value of light products to be calculated for any crude oil, the next step was to apply this analysis to the monthly throughput of the refinery. This involved considerable attention to details of procedure in order to avoid errors.

Firstly, the crude oil coming to the refinery was not only of varying quality as regards content of light oils, but was of two distinct types, paraffinous and non-paraffinous. This resulted in a considerable difference in the specific gravities of the different cuts and, where the yields of standard products depended on the specific gravity, a corresponding difference in the percentage obtained by analysis.

In order to get representative samples of the crude oil fed to the stills, careful samples of each tank were taken and the quantity of crude taken from each tank noted. These samples were kept until the end of the month and then separated into two types, paraffinous and non-paraffinous. In order to save work in the laboratory a composite sample was made up of each type of crude by blending the separate samples in ratios proportional to the amounts of crude oil represented by each.

Secondly, the monthly production of the various products is scarcely ever obtainable as a direct measurement from the refinery returns. The usual practice is to make up a balance-sheet which contains on the debit side the crude oil and products in stock at the beginning of the month and the crude oil delivered during the month, and, on the credit side, the crude oil and products in stock at the end of the month and the products shipped from the refinery during the month. Subtraction of the debit side from the credit side gives the amount of crude oil run and the quantities of the several products obtained from that crude oil.

Usually the existence of stocks of special products and unfinished products at the beginning and end of the month complicates matters, especially when these stocks entail further distillation in order to make finished products.

The establishment of a system of analysis as detailed above removed this complication, for special products and unfinished products could be analysed in the same way as a crude oil and their potential value expressed in the terms of the standard products.

So, in addition to the analysis of the crude oil, the control laboratory analysed all special and unfinished products in stock at the beginning and the end of the month and all special products despatched during the month.

In this way, each item in the monthly balance-sheet was converted into its equivalent of standard products.

The standard products given in the above specifications were naturally selected as covering the whole range of light oil distillation and as typical of the greater part of the products sold. The series covered the whole range of light oils without including any alternative products. All such were included as special products.

Special products were made in lesser quantities and generally in response to special orders. A few of these special products are given below, together with the method of their valuation in terms of standard products.

Aviation benzine.—This is producible from light benzine by the removal of part of the second cut. By distillation with the column it can be split up into No. (1) Cut and No. (2) Cut, but the percentage of No. (2) Cut is less than the 48 per cent. generally required for light benzine. Aviation benzine is therefore light benzine *minus* a certain amount of No. (2) Cut. No. (2) Cut, which is not required for light benzine, is used in the heavy benzine. A given weight, W, of aviation benzine is therefore valued at $(1+x)$ W. of light benzine *minus* x. W. heavy benzine.

Medium benzine.—This is generally a mixture of light and heavy benzines, and the proportions are readily ascertained by distillation with the column.

White spirit No. 2.—This is rather heavier than No. 1, and is easily split up by distillation with the column into x per cent. of No. 1 plus y per cent. of kerosine.

Kerosine distillate.—This is merely unrefined kerosine. Its value as kerosine is equivalent to 1 per cent. loss plus 99 per cent. refined kerosine.

The method of analysis having been explained, attention may be drawn to the balance-sheet incorporating the refinery results month by month. The form of balance-sheet is appended. The

figures given are not actual refinery figures, but are included as typical for a refinery running a series of continuous stills and re-running a considerable amount of the primary distillates. The percentage figures given in lines 18 and 20 are, however, actual percentages obtained as an average over several months' working, and the prices in line 21 are the actual mean values of the standard products averaged over the same period.

The greater part of it will be readily understood by anyone familiar with the usual monthly balance-sheets showing refinery operations. It will be noted that the total weight of each item forms the first column of figures. The second column, except in the case of line 19, gives the inevitable loss as found by analysis in converting to the equivalent of each product in standard products. The next six columns give the weights of standard products for each item, and the last column the total weight of each item expressed in standard products.

Particular attention is requested to lines 17 *et seq.* Line 17 gives the maximum rendiment of standard products as ascertained by the control laboratory analysis.

Line 18 gives the percentages of the several standard products as found by the analysis.

Line 19 gives the actual equivalent in standard products of the products made by the refinery during the month.

Line 20 gives the percentages made by the refinery.

Line 21 gives the mean prices received by the refinery for the standard products during the month.

Lines 22 and 23 give the values of standard products obtainable and obtained by the month's operations, with the totals of these in the last column.

Line 24 gives the monetary loss for the month due to the refinery not making the maximum value in the light oil distillation.

Line 25 gives the important information for which this work was instituted—namely, the *percentage of efficiency* of the light oil distillation.

Lines 26 and 27 give the actual and inevitable losses, and line 28 the difference or avoidable loss of material incurred during the month.

The result of several months' operations showed that the refinery was only making some 85 per cent. of the maximum value that was possible from the crude oil.

If the maximum value of products F.O.B. Refinery per ton of crude oil run was £2 13s. 3d., the value actually realised was only about £2 5s. The difference for a refinery running 1000 tons of crude oil daily amounts to £12,300 per month or about £148,000 annually.

Such a difference between actual and potentially attainable value naturally called for a careful scrutiny of the system of distillation in the refinery. The plant of the refinery was of the usual type, consisting of a range of continuous stills without fractionating columns. A considerable amount of redistillation was in practice, in that a crude benzine was taken off the main stills and afterwards rectified into light benzine, heavy benzine and white spirit. Generally, also, some re-distillation of the kerosine distillate was made, when analysis of the raw distillate showed this would be profitable. With all this re-distillation it had been assumed, prior to the institution of the above system of analysis, that a fairly close approximation to maximum value of products was being obtained. Fuel used was, of course, known to be high on account of the amount of re-distillation, but the loss of 15 per cent. of the maximum value was quite irrespective of lack of efficiency in the use of fuel.

It seemed apparent, after close study of the position, that the only way to obtain an approximation to the maximum value was by adopting, in the refinery, the system of cuts used in making the analysis, and blending the several cuts as indicated above. No other plan enabled such high values to be obtained.

The above cuts could not be made from the existing bench of crude oil stills, as it was impossible to avoid a large overlap. A system of distillation was required which would give the necessary cuts without overlap as shown by an Engler distillation. Even the installation of bubble plate columns on each still of the battery would not have the desired result, as it would require too much of reflux to ensure the thorough separation of each cut.

The only plant which could be expected to satisfy requirements was a pipe still, in which all the light oils were first vaporized, to be afterwards fractionated in suitable columns. Such a plant has since been installed, and the writer understands that the efficiency of the light oil distillation is now 97 or 98 per cent. When the saving of the cost of the re-distillation is taken into account with the increased rendiment obtained from the crude oil, the whole cost of the plant will be amortized in less than a year.

Although, perhaps, the benefit of the above system of making distillation cuts is more in the case of the rather stringent specifications required by the Rumanian market, the writer suggests that in the majority of cases the selection of cut points in accordance with the various temperatures given in the specifications of the different products, and the subsequent blending of these cuts to make the products will give a higher total yield than that obtained by taking the products themselves direct from the distillation plant. The latter method does not seem to give facilities for making the best use of the close fractionation rendered possible by modern methods of distillation.

MONTHLY BALANCE SHEET OF REFINERY.

		Actu Tons
Debit.		
1.	Crude Oil in Stock	17,30
2.	Crude Oil received during month	36,47
3.	Total Crude Oil Debit	53,78
4.	Stocks of Standard Products, 1st of Month	47,82
5.	„ Special Products, 1st of Month (Aviation Benzine and W.S.2. Distillate)	2,79
6.	„ Unfinished Products, 1st of Month	16,38
7.	Total Products Debit	67,00
8.	Total Debit (Line 3 + Line 7)	120,78
Credit.		
9.	Stocks of Standard Products, End of Month	42,76
10.	„ Special Products, End of Month (Medium Benzine) ..	1,23
11.	„ Unfinished Products, End of Month	13,26
12.	Sales of Standard Products during Month	35,52
13.	Sales of Special Products during Month (Aviation and Medium Benzine and W.S.2)	3,63
14.	Total Products Credit	96,40
15.	Stocks of Crude Oil	23,62
16.	Total Credit (Line 14 + Line 15)	120,02
17.	Crude Oil run during month (Line 3 — Line 15)	30,16
18.	Theoretic percentage of Standard Products	—
19.	Actual equivalent of Standard Products made (Line 14 — Line 7)	—
20.	Actual percentage in equivalent of Standard Products	—
21.	Mean value F.O.B. Refinery of Standard Products during Month	..
22.	Theoretic Value of Crude Oil run (Line 17 at prices in Line 21)	..
23.	Realised Value of Crude Oil run (Line 19 at prices in Line 21) ..	..
24.	Loss in Value (Total of Line 22 — Total of Line 23)	..
25.	Efficiency of Distillation during Month $100 \times \frac{\text{Total in Line 23}}{\text{Total in Line 22}}$	84·66%
26.	Percentage of Actual Loss	2·65%
27.	Percentage of Theoretic Loss	0·93%
28.	Avoidable Loss during Month	1·72%

...INERY.

	Actual Tons.	Loss.	L. Benzine.	H. Benzine.	W. Spirit Refined.
.. ..	17,302	144	3,078	804	1,613
.. ..	36,479	361	5,959	1,664	3,335
.. ..	53,781	505	9,037	2,468	4,948
.. ..	47,823	—	261	1,006	—
Benzine and Distillate)	2,798	6	817	297	1,242
.. ..	16,380	186	1,625	1,390	2,690
.. ..	67,001	192	2,703	2,099	3,932
.. ..	120,782	697	11,740	4,567	8,880
.. ..	42,760	—	1,079	124	—
Benzine) ..	1,230	—	282	948	—
.. ..	13,260	232	901	1,065	2,606
.. ..	35,523	—	3,393	1,424	828
and Medium d W.S.2)	3,630	—	1,216	372	1,116
.. ..	96,403	232	6,871	3,933	4,550
.. ..	23,620	224	3,867	1,108	2,071
.. ..	120,023	456	10,738	5,041	6,621
.. ..	30,161	281	5,170	1,360	2,877
.. ..	—	0·93	17·14	4·51	9·54
14 — Line 7)	—	799	4,168	1,834	618
.. ..	—	2·65	13·82	6·08	2·05
			£ s. d.	£ s. d.	£ s. d.
uring Month	.. ..		7 11 6	5 12 5	5 3 3
s in Line 21)	.. ..		39,162 15 0	7,644 6 8	14,852 10 3
Line 21) ..	.. ..		31,572 12 0	10,308 12 2	3,190 8 6
.. ..	.. ..	..	.. ..	.. ..	.. ..
in Line 23 / in Line 22	84·66%				
.. ..	2·65%				
.. ..	0·93%				
.. ..	1·72%				

T VALUES IN STANDARD PRODUCTS.

W. Spirit Refined.	Kerosine Refined.	Gas Oil.	Residue.	Total Products.
1,613	2,673	976	8,014	17,158
3,335	5,739	1,581	17,840	36,118
4,948	8,412	2,557	25,854	53,276
—	1,638	2,335	42,583	47,823
1,242	1,030	—	—	2,792
2,690	10,253	236	—	16,194
3,932	12,921	2,571	42,583	66,809
8,880	21,333	5,128	68,437	120,085
—	2,441	1,072	38,044	42,760
—	—	—	—	1,230
2,606	7,908	548	—	13,028
828	7,093	3,858	18,927	35,523
1,116	926	—	—	3,630
4,550	18,368	5,478	56,971	96,171
2,071	3,668	1,188	11,494	23,396
6,621	22,036	6,666	68,465	119,567
2,877	4,744	1,369	14,360	29,880
9·54	15·73	4·54	47·61	99·07
618	5,447	2,907	14,388	29,362
2·05	18·06	9·64	47·70	97·35

£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
5 3 3	2 8 11	1 13 2	0 6 7	
14,852 10 3	11,603 0 8	2,270 5 2	4,726 16 8	80,259 14 5
3,190 8 6	13,322 9 1	4,820 15 6	4,736 1 0	67,950 18 3
.. .. ..	.. ..	.. ..	.. ..	12,308 16 2

DISCUSSION.

The President said that the paper was an interesting one, and would appeal more particularly to those members more associated with refinery management. He would, however, like to ask one question : If one put into a refinery the modern bubble plate columns referred to, would the primary analysis still be carried out with the very inadequate fractionating plant described in the text?

Mr. James Kewley said that Mr. Ashworth had tackled a difficult subject and one to which sufficient attention had undoubtedly not been paid. That this question of evaluating a crude was a difficult one was indicated by the fact that neither the Americans nor ourselves had been able to agree a satisfactory method for a general evaluation of crude oil. The difficulty lay in the fact that no method of analysis was of much use in itself unless it bore a definite relation to the working of a particular refinery and the products which that refinery made. Naturally, refineries differ very greatly in that respect. He thought that the method which Mr. Ashworth had suggested was a very good one and that the fractionation was sufficiently adequate as the distillate cut at a certain temperature, when distilled in an A.S.T.M. flask, gave that temperature as the final boiling-point. The A.S.T.M. test was generally accepted as the standard method for estimating the boiling-point range of products, and the method seemed reasonable. The A.S.T.M. test did not indicate perfect fractionation. Many modern refinery plants yielded gasoline and kerosine which, when distilled by the A.S.T.M. method, showed no overlap, but actually a gap. Mr. Ashworth's method was, in principle, that of taking an initial cut at some point sufficiently low and then a number of other cuts at definite temperature or percentage intervals, which cuts, by suitable admixture, gave the products to be expected. Such a method is in use in many refineries for control purposes and for evaluating crude. This subject is an interesting one as crude is bought and sold and the question of settling the value is thus of great importance. The question of getting the best value out of the crude oil was a very difficult one, complicated because it was not possible to divide it by a series of cuts into hard and fast products. Kerosines and gasolines, for example, might have considerable overlaps in boiling-point ranges, and such was unavoidable. For example, a kerosine for use for power purposes would have to have a considerable fraction boiling below 200° C., although this might not be necessary if the kerosine were being used for illuminating purposes. He thought that some modification of the method which Mr. Ashworth had suggested might be of general applicability in the industry.

Mr. N. A. Anfilogoff said that in a way, presumably, it came within part of Mr. Ashworth's duty, but he (the speaker) would have had something different to say if he had been called in and asked his opinion about a refinery which had still got the "usual crude oil stills without any fractionating columns." He did not know that they were so "usual" to-day; he thought that they had been done away with 20 years ago. What would be of greater interest, perhaps, was to realise that the most efficient refinery was that which was the most efficient servant to the sales department. It was no use if a refinery worked from year to year and made nice little cuts, and did blending. The refinery must be subservient to the market. If a refinery had laid itself out, or had become laid out, to make certain cuts and produce a certain grade of spirit, another grade of light oil and another grade of kerosine, and could not do anything else except by blending, then that refinery ought to be "laid out" in another sense. One realised that kerosine, for instance, must have something like 40 or 50 per cent. boiling below 200° C., and it was necessary to have that quantity below 200° C., because otherwise you could not sell it as kerosine. With regard to its use as an illuminant one must not forget that there was such a thing as capillary attraction where wicks are used, and unless one had the lighter hydrocarbons one would not get the illuminant. If it was going to be used for motive power it was necessary to have some of the light hydrocarbons. More years ago than one might care to remember Messrs. Sommer and Rünge of Berlin put on the market a little distillation apparatus to all intents and purposes as described by Mr. Ashworth. While it used empirical figures of 150°, 275° and 315° C., and it did not use 1000 c.c., but only 100, it gave a "light oil value" for the crude. After all was said and done the question which was put to Mr. Ashworth was: "Is this refinery getting the maximum out of the crude oil run, and if not what proportion of the maximum value is it getting?" It could not get any values at all if it had not any fractionating columns. If it meant taking off the lighter distillates in the one still, whether it was a pipe still or any other one, and then having to redistil it all, you could not help losses, and you could not have efficiency. You could not have more than the amount which would distil up to, say, 315° C. Having got that did it really matter whether you split it up into a number of cuts, as suggested by Mr. Ashworth, or whether you took it off in one fell swoop in the laboratory as long as you were satisfied that you had provided a fractionating column which would take off all the lighter hydrocarbons boiling, say, at below 315° C., that is to say the gas oil. Having ascertained the maximum percentage of light oils that could be got out of the crude oil, surely it was a child's

work to split it into the required fractions. All that was wanted was the value of the light distillates within that crude. If you distilled it up to 315° C. you were going to get it. With regard to the rest in a refinery the man who was looking after the business end of the distillation, that is to say the tail-house man, did not look at temperatures, but he went by specific gravity. He was told that from such a specific gravity to such a specific gravity he had to run it in such and such a blend, and so on. The blends were, of course, done by the control chemist in charge of the refinery. Might he suggest to Mr. Ashworth that the easiest way in which to get the maximum "light oil value" in the crude, and at the same time obtain the sp. grs. at which to make the cuts would be to carry out a laboratory distillation in 2½ per cent. fractions all the way down, and to test each 2½ per cent. fraction. If the distillation was larger, one could take even smaller fractions and test them for specific gravities, and note the temperatures at the same time. The temperatures would be useful to the chemist; the specific gravities would be useful to the tail-house man. He was not an accountant by profession, but so far as accountancy was concerned he suggested that the less one complicated it the better. If you were going to have a refinery which would work for twelve months without stopping, did it so much matter what the month end figure was, and did it necessitate testing and analysing the half finished products in order to get such an accurate result for the month end? Why not regard the contents of the stills and plant as "crude" at each month end? He had already dealt with the part of Mr. Ashworth's paper which said: "The plant of the refinery was of the usual type, consisting of a range of continuous stills without fractionating columns." Lower down in his paper Mr. Ashworth said: "The only plant which could be expected to satisfy requirements was a pipe still, in which the light oils were first vaporised, to be afterwards fractionated in suitable columns." He was afraid that if he were on the governing body of a company which owned a refinery, and the refinery manager suggested that the best way in which to do the work was to distill it first and then have to redistil it and refractionate it, he would want to take this gentleman for a quiet walk round the still waters.

Mr. Ashworth, in reply, said that Dr. Dunstan had asked whether the rather crude laboratory apparatus would be retained in a case when the refinery was working with proper bubble plate columns. As a matter of fact the cuts were fairly close, that is to say, if one cut at 200° C. there was very little boiling at over 200° C. in that cut. Of course, this apparatus was devised to get a standard to use which would be very much better than

anything which had been used before. He did not think that it was put forward as being the final form of analysis which might be necessary in the case of a refinery working with a thoroughly efficient apparatus.

In answer to a question by the President, Mr. Ashworth said that he had not tried the Peter's column. The gain to be obtained by using a much more efficient apparatus in the laboratory seemed comparatively small. First of all, this was the institution of a new system. One did not want to make complications. Doubtless in the future if the refinery operation approached too closely to the laboratory analysis, they would stiffen up the laboratory analysis by using a Peter's column or something similar to it.

In reply to Mr. Kewley, and also to Mr. Anfilogoff, with regard to kerosine, he thought perhaps there was a misunderstanding when he read the method of combining and getting the kerosine. The kerosine was not confined to the cut above 200° C., but the balance of Cut No. 4 which was not used up in making white spirit was put into the reservoir and formed the initial part of the kerosine cut. In that way the initial point of the kerosine would be 175° C. approximately.

Mr. Anfilogoff had asked rather a lot of questions. The first one was, was the refinery subject to the sales department or was the department to sell what the refinery could make ? If the sales department could be on the top, the refinery would have to conform its practice to suit the sales department ; if not the refinery should dictate. He thought that he had answered the question with regard to the initial boiling point of the kerosine. He did not quite follow why the total amount of the light distillate obtainable from the crude was sufficient to give the refinery all that it wanted to know about the maximum value. He tried to show in the paper that by various ways of combining the light cuts a certain maximum value was obtained which was not obtained before, although the refinery was presumably taking off the same amount of light distillate in its light oil distillation. With regard to the control by the still-man doubtless that would continue to be by gravity, but the gravities would be dictated to the still-man by the control chemist, and the control chemist would obtain those gravities which he instructed the still-man to take off from his own laboratory analysis. With regard to monthly reports he could only say that the refinery at which he was working preferred to know what it was doing month by month, instead of waiting until the end of the year to find out whether it had done well or badly. He thought that there was perhaps a little misunderstanding with regard to the system of distillation by pipe still. Where he talked of the pipe still, where all the light oils were first

vaporised, he did not presume that those vapours were going to be condensed and redistilled to form these different cuts. The total vapours were passed to the bubble column, and they were fractionated and condensed into the required cuts. He thought that he had to the best of his ability answered all the questions which had been put.

On the motion of the President, a very hearty vote of thanks was accorded to Mr. Ashworth for his interesting paper.

The Chemical Examination of Gasolines and Light Mineral Oils.*

By Donald A. Howes, Ph.D., B.Sc. (Associate Member).

Introduction.

The subject of the chemical analyses of gasolines and light mineral oils is one that has received a great deal of attention during the past few years, chiefly because of the fundamental difficulties encountered. Much work has been published on the subject, some of which is of real utility and some of which is so conflicting and even contradicting as to be of little value.

From the present review of the literature on this subject it is evident that one real cause of the unsatisfactory state of hydrocarbon oil analysis is the fact that the chemistry of pure hydrocarbons is a neglected chapter in organic chemistry. Very few hydrocarbons of unquestionable purity (except those of the aromatic series) have been examined in detail, and what little work has been done has been conducted on substances of doubtful purity, with the result that much contradictory information is published.

The present review is an attempt, not to suggest new methods of gasoline analysis nor yet to clear up conflicting statements, but to collect into one paper the most important analytical methods that have from time to time been proposed; briefly to describe, examine and criticise them.

The paper is divided into three parts, dealing with the estimation of unsaturated, aromatic, and naphthene and paraffin hydrocarbons.

The Estimation of Unsaturated Hydrocarbons.

The determination of unsaturated hydrocarbons may be accomplished by:—

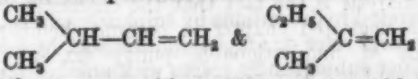
(1) Solution in sulphuric acid.
(2) Absorption of the halogens.
(3) Reactions with mercury salts.
(4) Reaction with ozone.
(5) Oxidation with perbenzoic acid.
(6) Reaction with thiocyanogen.
(7) And by other methods.

* Paper received December 10, 1929.

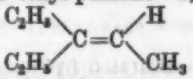
1. *Estimation by Means of Sulphuric Acid.*—It is generally known that unsaturated hydrocarbons are acted upon by sulphuric acid of lower concentration than is necessary for the attack of aromatic and other hydrocarbons, and this fact has long been used to effect a very rapid and convenient, if not accurate, analytical method.

The chemical reactions involved are complex, in as much as the products of the reaction under different conditions are alcohols, mono- and dialkyl esters and polymers. The action of sulphuric acid on unsaturateds depends to a large extent on the molecular weight and molecular composition of the latter and on the strength of the acid employed.

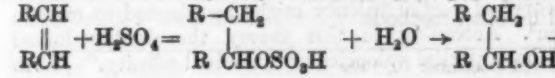
The tendency of the olefines and substituted ethylenes to react with sulphuric acid is distinctly less than their tendency to react with bromine, but the substitution of electro-positive groups, such as methyl groups, results in greatly increased activity. Isobutene $(CH_3)_2 C{=}CH_2$, is rapidly and completely dissolved by 63 per cent. sulphuric acid at 17° C., and tetramethyl-ethylene $(CH_3)_2 C{=}C (CH_3)_2$ reacts completely with 77 per cent. acid at ordinary temperatures. Of the two pentenes



the latter dissolves more readily in 66 per cent. acid.[1] Michael and Brunel believe that in the aliphatic series the tendency to form alcohols and alkyl sulphuric esters decreases with increasing molecular weight, this result appearing to be at a maximum with the pentenes and the hexenes. This belief is shared by Brooks and Humphrey[2], who have shown that polymerisation of the olefines of higher molecular weight may be preceded by alcohol formation. The difference in the final result may therefore be due in large part to the relatively greater stability of the simpler alcohols. Thus, under the same conditions, 3 ethyl pentene—2,



yields 72 per cent. alcohol and 12 per cent. polymers, while 2-methyl undecene-2 yields 97 per cent. polymers and only a trace of alcohol. Secondary octyl alcohol, when treated with 85 per cent. sulphuric acid at 20° C., gives a yield of octene polymers $C_{16} H_{32}$ and $C_{24}H_{48}$ increasing with the time of standing. The mechanism of these changes is obscure, but it has been assumed that the alcohols formed are the result of the hydrolysis of the alkyl sulphates first formed :—



This, however, cannot be the case, since the mono sulphuric esters of the pentenes, hexenes and heptenes only undergo very slow hydrolysis even at 100° C. The highest yields of alcohols are obtained using sulphuric acid which contains water, more alcohol being formed with 85 per cent. acid than with 95 per cent. acid, or with benzene sulphuric acid.

To account for this Brooks and Humphrey[2] have proposed that the formation of alcohols in cold solutions is due to reaction with the monohydrate of sulphuric acid, $H_2SO_4H_2O$, or higher hydrates.

It is practically certain that esters of this acid have quite different degrees of stability, and quite different rates of hydrolysis, from the known relatively stable esters of ordinary sulphuric acid.

The chemistry of polymerisation has received attention at the hands of Morrell[3], Brooks and Humphrey (*loc. cit*), and Joubert and Norris[4]. Brooks and Humphrey found that the polymers were more stable to sulphuric acid than the parent olefines, but still contained a double bond. These polymers are not removed in the acid sludge in refining, but remain largely in the oil layer—*i.e.*, in the refined oil. One assumption about the mechanism of polymerisation of unsaturated hydrocarbons by sulphuric acid is the formation at first of the acid ester or alkyl sulphuric acid by addition. This addition product subsequently reacts with another molecule of the olefine to form the polymer. The sulphuric acid is liberated and theoretically may go through many cycles[5]:—

(1) $(CH_3)_2C{=}CH_2 + H_2SO_4 \rightarrow (CH_3)_2C(O{-}SO_3H){-}CH_3$

Iso-butene — Iso-butyl sulphuric acid.

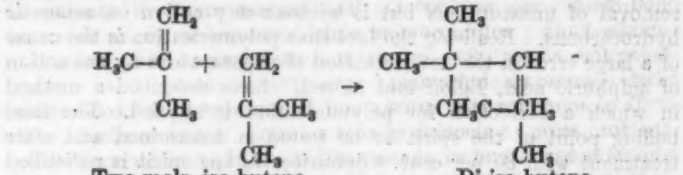
(2) $(CH_3)_2C(O{-}SO_3H){-}CH_3 + HHC{=}C(CH_3)_2$

$\rightarrow (CH_3)_2C(CH{=}C(CH_3)_2){-}CH_3 + H_2SO_4$

Di-iso-butene (or iso-octene)

Thiele's theory[6] of partial valency might be adapted to explain polymerisation[3]. According to this theory the doubly linked carbon atoms have partial valencies or "residual affinity." With

this assumption the following mechanism of the reaction may be postulated:



Two mols. iso-butene — Di-iso-butene

The further assumption is made that the molecules contain a mobile or labile hydrogen atom which shifts from one molecule to the other, thus permitting polymerisation. According to either of the above theories, two unlike molecules may also react, thus explaining the formation of all the higher polymers. Ormandy and Craven[6] assert that the so called "polymers" of olefines are in reality paraffin hydrocarbons and they state that these compounds are fully saturated. In these views they are not supported[7].

It will thus be seen that sulphuric acid cannot be used for the accurate determination of unsaturated hydrocarbons. The polymers are not removed by the acid and hence quantitative results cannot be obtained. The sulphuric esters, being soluble in the residual spirit stay therein also, and are not removed by the acid; the alcohols alone are removed.

Therefore if sulphuric acid is used for such a determination, it must be of sufficient strength to dissolve the stable polymers formed by its own action, yet be without action on hydrocarbons of other groups, especially the aromatics. As will be shown later this presents great difficulties.

Ormandy and Craven[8] treated petrols with sulphuric acid of various strengths and found that the density and refractive index of the residual spirit after acid treatment rose until the acid strength reached 88 per cent. This they ascribed to polymerisation and removal of unsaturateds. At higher strengths of acid, extraction of aromatics occurred and the density and refractive index fell to lower values.

Moore and Hobson[9] found that 88-90 per cent. acid was essential for the complete removal of unsaturateds while Riesenfeld and Bandte[10] state that 92-94 per cent. acid is required. Sulphuric acid of this strength will however, remove aromatic hydrocarbons, for instance, according to Reuter[11], m-xylene is soluble in such acid of only 80 per cent. strength.

Kattwinkel[12] has found that the action of sulphuric acid could be moderated by the addition of boric anhydride and accelerated by the addition of phosphorous pentoxide. He claims that

sulphuric acid, sp. gr. 1·84, to which has been added boric acid in the proportion of 5 grams to 100 c.c. of acid, effects the complete removal of unsaturateds but is without any action on aromatic hydrocarbons. Realising the fact that polymerisation is the cause of a large error in the determination of unsaturateds by the action of sulphuric acid, Egloff and Morrell[13] have described a method in which a correction for polymerisation is applied. The final boiling point of the spirit to be tested is determined and after treatment with 80 per cent. sulphuric acid the spirit is redistilled to this temperature. The residue, which consists of polymerised hydrocarbons, is added to the loss to acid and the total is taken as the percentage of unsaturated hydrocarbons originally present. This correction, however, is only approximate, for some unsaturateds might be polymerised to hydrocarbons boiling at a temperature below the original final boiling point of the spirit and would therefore not be measured in the residue. For example, trimethyl ethylene, B.P.38°, polymerises to a mixture of diamylenes boiling between 150 and 160° C., whereas the final boiling points of the petrols sold in English markets are in the immediate neighbourhood of 180° C.

The dipolymers of the hexenes boil between 190° and 200° C., whereas the dipolymer of iso α heptene has a boiling point of 220-224° C. and a mixture of octene—1 and octene—2 gives a mixture of dipolymers boiling between 275° and 285° C.

In the case of a cracked spirit Houghton and Bowman[14] found that sulphuric acid of 91 per cent. strength produced the maximum amount of polymerisation.

Besides such phenomena there is another complication attending the use of sulphuric acid for the quantitative estimation of unsaturated hydrocarbons. It was observed by Kramer and Spilker[15] that in the presence of concentrated sulphuric acid, styrene and the xylenes condensed to form styro-xylenes. Later Brochet[16] found that aliphatic unsaturated hydrocarbons condensed with benzene homologues in the same fashion, *e.g.*, benzene and hexene give hexyl benzene. Toluene and xylene behave in the same way and other unsaturateds probably react like hexene.

Brame[17] conducted a few experiments to determine whether similar condensations took place when petrols and synthetic mixtures were shaken with sulphuric acid of strengths which are generally used for the estimation of unsaturateds. He found that when 85 per cent. acid was used, 30 per cent. of the aromatics originally present in a petrol were removed while when 88 per cent. acid was employed over 50 per cent. was removed. The results of his experiments are, however, not conclusive, for Brame did not ascertain whether acid of either 85 per cent. or 88 per cent. had any

action on aromatics alone, although they do indicate that condensations of the type described by Brochet probably take place. Unsaturated hydrocarbons containing more than one double bond are more easily polymerised than mono-olefines. Thus allylene in contact with concentrated sulphuric acid yields trimethylbenzene and crotonylene gives hexamethyl benzene. Cyclic unsaturated hydrocarbons can react with sulphuric acid to form other hydrocarbons. Thus methylcyclohexene gives methylcyclohexane and two isomeric diheptenes; some toluene is formed at the same time[18]. Dimethylcyclohexene yields dimethylcyclohexane, two dioctenes, and a little xylene. It is thus apparent that sulphuric acid is quite unsuitable as a reagent for the quantitative determination of unsaturated hydrocarbons. Owing to polymerisation a strong acid is required—acid of such a strength that it attacks aromatics, and also new hydrocarbons, other than polymers are formed.

2. *Methods of Estimating Unsaturated Hydrocarbons depending on Absorption of the Halogens.*—By virtue of the double bonds which they contain, unsaturated hydrocarbons readily absorb the halogens, chlorine and bromine, to form dichlorides and dibromides, the reaction being a simple addition process. In aqueous solution, however, part of the halogen will react with the water giving a hypo-acid which adds on to the olefine to produce a halogen derivative of an alcohol, thus :—

$$R\,CH{=}CH_2 + H\,Br\,O \rightarrow R\,CH\,Br{-}CH_2OH$$

When simple addition of two halogen atoms takes place a simple titration will indicate the "double bond equivalent" of the unsaturateds present and from this may be obtained an approximate figure for the "unsaturation" or unsaturated hydrocarbon content of the spirit under examination. The halogens used are generally bromine and iodine, and the results are expressed as bromine or iodine "numbers," *i.e.*, the number of grams of halogen absorbed per 100 grams of spirit. Such an evaluation is purely empirical and conveys but little, a knowledge of the molecular weight of the unsaturateds present being essential before an accurate interpretation is possible.

The reaction is complicated by the fact that substitution of hydrogen atoms often proceeds at the same time as halogen addition, as is shown by the evolution of hydrogen bromide. The ease with which substitution occurs probably increases with rise in the molecular weight of the hydrocarbon reacting. Davis has recently published[19] an interesting account of work on the bromination of the olefines, particularly in carbon tetrachloride solution. He found that, contrary to general belief, ethylene brominates in this

solvent at a rate measurable with time, and that if the solutions are dried and kept away from bright light, the reaction takes hours, and even days, for completion. Traces of moisture speed up the reaction whereas added hydrogen bromide does not affect it, and it was also found that the rate of the dark bromination of ethylene in dry carbon tetrachloride increases progressively as the temperature is lowered from 25° to 0° C. Davis suggested that the bromination in this case proceeds mainly through a bromine hydrate and that the concentration of this hydrate increases as the temperature is lowered from 25° to 0° C. Davis also observed that temperature has but little effect on the dry bromination of trimethylethylene or di-isobutene, and that large amounts of hydrogen bromide are evolved in these two cases.

The iodine number methods for the estimation of unsaturation devised by Hubl[20] and Wijs[21] are of great use in the examination of animal, fatty and vegetable oils, but soon proved themselves not to be applicable to the examination of mineral oils and petroleum distillates. That due to Hubl makes use of a solution of iodine and mercuric chloride in alcohol, but in practice it proved very inconvenient and gave discordant results. The method of Wijs utilises a decinormal solution of iodine monochloride in glacial acetic acid; this solution, though needing special preparation, will keep for a long time. Neither of these methods are now much used. The method of Hanus[22] possesses many advantages over the older methods, indeed Dean and Hill[23] consider it to give better results than the bromine number method of McIlhiney[24]. Garner[25] has used a modified form of the Hanus method for the estimation of the unsaturateds in cracked spirits. The Hanus solution consists of a mixture of equivalent weights of bromine and iodine dissolved in glacial acetic acid and the method is quite capable of giving accurate results providing certain factors (which will be described later) are kept constant.

Radcliffe and Polycronis[26] have studied the action of Hubl, Hanus and Wijs solutions on heavy mineral oils. They found that the numbers obtained were in the order Hanus–Wijs–Hubl, although the Hanus and Wijs values agreed fairly closely. The Hubl solution gave an iodine number much below the theoretical value for an amylene at the end of two hours, while the Wijs solution gave a satisfactory number. With regard to the Hanus method, Smith and Tuttle[27] have pointed out that the iodine number of an oil increases as the excess of Hanus solution is increased, and this has been confirmed by Morrell and Egloff[28], who have also noticed that by keeping the relative amounts of oil and Hanus solution constant, using the same oil, the iodine number is almost constant. Their results are reproduced in Table 1.

TABLE I.

The Effect of Constant Proportion of Oil to Hanus Solution.

	Oil. g.	Hanus solution. c.c.	Iodine No.
(*a*)	0·25	45	77·8
	0·15	27	78·0
(*b*)	0·10	20	82·6
	0·15	30	82·4
	0·25	50	83·1
(*c*)	0·125	30	88·6
	0·15	36	87·7
	0·25	60	88·7
(*d*)	0·08	30	111·4
	0·16	60	111·8
	0·24	90	111·3

Faragher, Gruse and Garner[29] examined the Hanus method when applied to pure unsaturated hydrocarbons. The results obtained are interesting. It was found that in the case of mono-olefines theoretical absorption of iodine from the Hanus solution was obtained; with diolefines however, and also with heptine, an acetylenic hydrocarbon, the maximum absorptions obtained only corresponded to the amount of iodine that would have been required if the hydrocarbons had been mono-olefines. Thus with hexadiene and isoprene the maximum absorption of iodine obtained in each case was 425 whereas the theoretical maximum absorptions are 630 and 741 respectively. Faragher, Gruse and Garner also found that the iodine numbers of gasolines obtained by this method were practically unaffected by changes in the relative proportions of spirit and Hanus solution. They also state that the Hanus reagent does not cause any appreciable substitution of hydrogen atoms in the molecules of simple paraffins, cycloparaffin or aromatic hydrocarbons, or of straight, branched chain or cyclic olefines, of diolefines acetylenes or cracked gasolines.

Johansen[30] states the diametrically opposite case, that the iodine absorption as obtained by the Hanus solution is a combined addition and substitution value, and by employing a modified solution in which the iodine bromide is dissolved in the neutral solvent carbon-tetrachloride, instead of in glacial acetic acid, he was able, by means of a modification of the method due to McIlhiney[24] to discriminate between these addition and substitution values, and to show that substitution played a very considerable part in the absorption of iodine from Hanus solution by mineral and fatty oils. Morrell and Egloff[31] check all the findings of Johansen within certain limits and show that there is a considerable change in the addition values with change in the relative proportion of the reactants, although this change is not nearly so great as the variation in the substitution values, and they show that in the cases of certain oils negative addition values are obtained.

Regarding the time factor in iodine number determinations Smith and Tuttle (*loc. cit.*), in observations on the Hanus method, point out that after 15 minutes little or no effect is observed on the amount of iodine absorbed, whereas the effect of temperature is much greater than that of time and becomes even more pronounced with increased excess. Dean and Hill (*loc. cit.*) recommend a thirty-minute reaction period and a graduated excess of Hanus reagent calculated so that only 10–30 per cent. of the available iodine is absorbed.

Miskin[31] found that increasing the period for cracked gasolines has the same result as an excess of reagent—namely, an increase in the iodine number.

In the Report of the Benzol Research Committee for 1924 are to be found results of experiments which were conducted to determine what effect, if any, the solvent had upon the quantity of iodine absorbed, when Wijs solution was employed. Varying amounts of acetic acid, chloroform, carbon tetrachloride, and carbon disulphide were added to the reaction mixture and the corresponding effects upon the iodine absorbed recorded. These results are tabulated in Table II.

TABLE II.

The Effects of Solvents upon Iodine Numbers (Wijs).

Solvent. c.c.	Iodine numbers. Acetic acid.	Chloroform.	Carbon tetrachloride.	Carbon disulphide.
0·0	6·28	6·30	6·28	6·3
2·0	6·08	6·22	5·90	5·85
5·0	5·85	6·14	5·48	5·41
10·0	5·61	6·02	4·74	4·65
20·0	5·20	5·62	3·88	3·90

From these figures it is evident that the retarding action of the solvent is something more than a mere diluent effect, lowering the concentration of the iodine in the reaction mixture. The four solvents behave very differently although they are all completely miscible with acetic acid over the ranges examined and no appreciable volume changes occur on mixing them; the concentration of iodine in the mixture for a given addition of solvent is, therefore, the same for each of the four solvents. The results show that the nature of the solvent has undoubtedly a specific action upon the iodine and that this effect is increased by the greater amount of solvent used.

The bromine number method of McIlhiney[24] is the most suitable for the separate measurement of halogen addition and substitution, and depends upon the fact that for each atom of hydrogen replaced by bromine, one molecule of hydrogen bromide is formed. By estimation of this free acid, therefore, as well as the total amount

of bromine absorbed, data are obtained for calculating both the bromine taken up by direct addition (during which hydrobromic acid is formed), and the bromine taken up by substitution. The estimation of the hydrobromic acid is accomplished by the addition of potassium iodate to the solution after the excess bromine has been destroyed by potassium iodide and sodium thiosulphate. The reaction involved is $KIO_3+5KI+6HBr=6KBr+3H_2O+3I_2$, which is not brought about by the common organic acids. Experiments described in the First Report of the Joint Benzole Research Committee show that a gradually increasing total bromine absorption is obtained as the reaction period is prolonged, exactly as is obtained in the case of methods using iodine, but that the addition value is unaffected. The substitution reaction is a slow, continuous one and proceeds as long as any free bromine remains in the reaction mixture.

The McIlhiney method is capable of concordant and accurate results with light spirits providing the experimental conditions are kept identical in each determination, but Dean and Hill[33] and Morrell and Egloff[28] have experienced more difficulty in obtaining consistent results with bromine number methods than with those using iodine.

Waterman, Spijker and Westen [32] and Waterman and Westen[33] have shown that the McIlhiney method is capable of giving results that agree with the theoretical values for pure unsaturated hydrocarbons, *e.g.*, cyclohexene and amylene.

The bromine number method of Francis[34] is noteworthy. It employs a standard solution of potassium bromide and potassium bromate, which in acid solution generates bromine,

$$KBrO_3+5KBr+3H_2SO_4=3K_2SO_4+3H_2O+3Br_2$$

the rate depending upon the strength of the acid. By making the solution only slightly acid the bromine can be generated slowly—and by vigorous shaking this is consumed by the double bonds fast enough to keep it at very low concentration and thus avoid substitution reactions. This is important for reliable results. The fact that mineral oils do not mix with the reagents is no disadvantage and may be desirable in avoiding substitution, but it does necessitate vigorous shaking. It makes no difference in the titration whether dibromides or bromohydrins are formed, as may by seen from the following equations:

$$RCH=CHR^1+Br_2+H_2O\rightarrow\begin{cases}RCHBr—CHBrR^1+H_2O\\ RCHBr—CHOHR^1+HBr\end{cases}$$

Bromide-bromate has been used previously for the estimation of unsaturation. Frank[35] used it in carbon bisulphide solution and Utz[36] made use of a chloroform solution of the bromide and titrated

it against an aqueous solution of the bromate. Weger[37], Graefe[38] and Routala [39] also used bromide-bromate solutions.

Up to the present little work has been published on the results obtained by the use of the Francis method, but the Author has found it capable of concordant, if not accurate, results although it does not possess the convenience of the McIlhiney and Hanus methods. Cortese[39a] tested the method with pure, unsaturated hydrocarbons of various types and reached the conclusion that it gives reliable results for aliphatic olefines and diolefines whether conjugated or not, but only approximately correct results for certain ring structures. The advantages of halogen absorption methods, as compared with those in which sulphuric acid is used for the estimation of unsaturation, consists in that polymerisation and condensation are avoided. On the other hand, there is evidence that under the experimental conditions employed hydrocarbons other than unsaturated hydrocarbons are attacked. Gustavson[40] found that dry bromine attacked benzene, whilst moist bromine containing hydrobromic acid possessed a far more energetic reaction upon it. Accordingly, if Gustavson's findings are correct, the method of Francis, using aqueous bromide-bromate solution should give more inaccurate results than that of McIlhiney. The capability of reacting with bromine increases in the case of the higher homologues of benzene, thus even with efficient cooling bromine acts upon amylbenzene and more rapidly upon amyltoluene and amylxylene[41].

Bromine also reacts with a few naphthenes. According to Gustavson (*loc. cit.*), dry bromine acts slowly upon trimethylene and the reaction is accelerated by the presence of water and hydrobromic acid. According to Tanatar[42], trimethylene bromide and propyl bromide are formed. The substituted cyclopropanes are attacked more readily[43]. Cyclobutane is stable towards bromine in chloroform solution[44] and the cyclopentanes and cyclohexanes behave likewise[45].

It will therefore be seen that there are many objections attendant to the use of the halogens in quantitative methods for the determination of unsaturated hydrocarbons. In the first case, iodine numbers or bromine numbers possess no absolute significance, and they are quite empirical; the molecular weights of the olefines reacting must be known before these figures can be used to calculate "percentage unsaturated content." Secondly, diolefines and acetylenes react towards iodine, and probably towards bromine, too, not as such, but as mono-olefines. Therefore their presence cannot be detected by these methods. The effects of time and concentration are complicating factors and the possibility of bromine and iodine reacting with aromatic and naphthene

hydrocarbons, especially when in aqueous solution, places these methods upon very unsafe foundations.

The obvious conclusion therefore is that iodine and bromine number methods must be used with very great caution in the estimation of unsaturated hydrocarbons in petroleum distillates.

3. *The Use of Mercuric Salts for the Estimation of Unsaturated Hydrocarbons.*—Unsaturated hydrocarbons react with mercuric salts in two ways, either they are oxidised or else they form complex addition compounds with the salts. The gaseous olefines easily form complex mercury compounds[46], from which they may be recovered by the action of acid. Unsaturated hydrocarbons of low molecular weight react easily at ordinary temperatures, but those of higher molecular weight—*e.g.*, octene and diamylene, react only slowly on boiling.

Tausz[47] found that cyclohexene, methyl cyclohexene and the terpenes also gave compounds with mercuric acetate while fully saturated hydrocarbons gave no reaction, and upon these observations he based a method for the quantitative determination of unsaturated hydrocarbons in the presence of the latter. According to the procedure of Tausz the spirit to be analysed is first of all shaken with a saturated solution of mercuric acetate to oxidise the most reactive unsaturateds, and then, to attack the more resistant ones, the spirit is refluxed with the reagent. When the reaction is complete the residual spirit is washed successively with aqueous caustic soda and sodium bisulphite solutions. The difference in volumes of the original and residual spirit represents the olefine content removed. This method was tested by Tausz using synthetic mixtures of pure hydrocarbons, and his results are reproduced in Table III.

TABLE III.

	Mixture of hydrocarbons.		Found saturated, c.c.		
	Unsaturateds.	Saturateds.	*a.*	*b.*	*c.*
1.	5 c.c. Amylene	45 c.c. Hexane	44·75	44·90	44·70
2.	10 c.c. „	40 c.c. „	39·80	39·75	39·90
3.	5 c.c. Hexene	45 c.c. „	44·80	45·00	44·85
4.	2 c.c. Heptene	18 c.c. Heptane	17·90	18·00	17·85
5.	5 c.c. Cyclohexene	45 c.c. Cyclohexane	44·70	44·75	44·90
6.	10 c.c. „	40 c.c. Hexane	39·75	39·90	39·85
7.	5 c.c. Methyl cyclohexene	45 c.c. Heptane	44·90	44·70	44·70

Balbiano and Paolini[48] also tried to estimate the olefines in American petroleum ether by this method, but in the course of their investigation failed to isolate the complex mercury compounds of amylene and hexene. Tausz[49], however, was able to obtain these compounds.

Brame and Hunter[50] describe their attempts to use the reaction between mercuric salts and olefines for the identification and separation of the latter from a cracked spirit. They abandoned the method in favour of a procedure involving bromination because they were unable to obtain good yields of hydrocarbons from the addition compounds with mercuric salts and also because they found that many of the unsaturateds, instead of forming addition compounds, were oxidised and destroyed.

Hugel and Hibou[51] have, as a result of their extensive work on the addition compounds of olefines with mercuric salts, shown that the method described by Tausz[47] is unsound. These workers found that for any given unsaturated hydrocarbon the addition compounds with mercuric salts have a variable composition, according to the conditions of the experiment in which they are formed. They also observed that while the higher olefines only react slowly if not at all in aqueous solution (although the reaction may be speeded up in alcohol solution)[52], olefines in which the double bond carries four alkyl radicals—*e.g.*, tetramethylethylene, definitely do not react. Therefore, the reaction is not applicable to all unsaturated hydrocarbons.

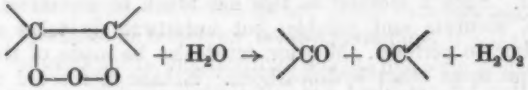
Hugel and Hibou have, however, published an outline of a method for the determination of such hydrocarbons, using mercuric acetate, which they are confident will give reliable results[51].

The hydrocarbon mixture is, according to this method, treated with a solution of mercuric acetate in glacial acetic acid, whereupon the unsaturateds present dissolve to form complexes with the mercury salt, and the volume of unabsorbed hydrocarbons is measured. The saturated hydrocarbons are not, however, completely insoluble in the acetic acid, and their solubility is yet increased by the solution in the acid of the unsaturated hydrocarbons, but may be rendered negligible by the prudent addition of water, in such quantity that the mercury complexes are not precipitated. The unsaturated hydrocarbons may be recovered by the addition of hydrochloric acid, or the complexes may be precipitated by the addition of water, and the olefines regenerated therefrom by dissolving in ether. Generally speaking, unsaturateds may not be quantitatively estimated by mercury salts except in special cases. The method seems to be inapplicable to high boiling fractions, and as has been mentioned before, some unsaturateds even of low boiling point do not react. The method must therefore be used with caution until more precise details concerning it are available.

4. *The Estimation of Unsaturated Hydrocarbons by Means of Ozone.*—It is well known at the present time that unsaturated

hydrocarbons are readily acted upon by ozone to form ozonides, and that these compounds may, in general, easily be decomposed to water soluble substances. At first experimental difficulties rendered the production of the ozonides, even of the simple olefines, impossible for a long time (*cf.* Schonbein[52] and Hautefeuille[53]), for the gaseous olefines explode even at very low temperatures in the presence of ozone, while amylene and hexene take fire. After many unsuccessful experiments Harries and Hafner[54] succeeded in preparing the ozonides of propylene, amylene and hexene by greatly diluting the hydrocarbon with a low boiling solvent that was indifferent towards ozone. Ethylene ozonide was prepared in the same way by Harries and Koetschan[55].

The true character of the reactions involved was first made clear by Harries[56], who showed that the initial products, which were thick viscous explosive substances, contained O_3 for each double bond present in the original hydrocarbon. These ozonides can break down in two ways as follows :—(1) By reaction with water to form hydrogen peroxide and ketones and aldehydes accompanied by complete rupture of the double bond :—



(2) Decomposition can take place on warming or in solvents such as absolute alcohol or glacial acetic acid in the absence of water to give a true peroxide and a ketone or aldehyde :—

The reaction of substances containing ethylene bonds with ozone is substantially as general a reaction as is the reaction with bromine. The ozonides of cyclic olefines are also easily prepared.

In view of the ease with which unsaturated hydrocarbons react with ozone, it is not surprising to find that methods for the quantitative estimation of the former have been devised based upon this reaction. The first work on the treatment of petroleum distillates was done by Molinari and Cucini[57] and Molinari and Fenaroli[58]. The last named investigators obtained from a Russian kerosine fraction, B.P. 295–300°, a yield of 32 per cent. of an ozonide, and suggested for the estimation of unsaturated hydrocarbons a method in which these are converted into ozonides and their decomposition products.

Danaila, Andrei and Melinescu[59] have recently described a similar method which they claim gives accurate and reliable results with light oils and spirits containing less than 5 per cent. of unsaturated hydrocarbons. According to their procedure oxygen is passed successively through a gas meter, a sulphuric acid wash bottle, a single element Siemens-Halske ozoniser and a wash bottle containing 35–40 c.c. of the oil and 30–40 c.c. of 30 per cent. aqueous caustic soda, cooled to −10 to −15° C. After the gas has passed through the oil for six hours at a rate of 4—14 litres per hr. the mixture is distilled in steam and the distilled oil washed with caustic soda and sodium bisulphite solutions and water, and finally dried over sodium. The difference in the losses to 98 per cent. sulphuric acid which the original oil and the oil after treatment undergo is equivalent to the unsaturated content. A modification in the above procedure is suggested[60] for oils non-volatile in steam; in this case they are not steam distilled but their volume is measured after washing with the usual reagents and drying, and the loss in volume due to the ozone treatment is taken as the content of unsaturated hydrocarbons originally present. Such a method as this has much to commend it; it is simple, accurate and reliable, but unfortunately takes rather a long time to perform. Mention must also be made of the action of ozone upon other hydrocarbons. Ethane is reacted upon by dilute ozone at 100° C., the initial oxidation products being ethyl alcohol and acetaldehyde[61], and benzene forms a highly explosive triozonide $C_6H_6O_9$. Naphthalene also is attacked by ozone. According to Tausz[62] the aliphatic hydrocarbons in the presence of aromatic hydrocarbons are attacked by ozone at ordinary temperatures.

In the method of Danaila, Andrei and Melinescu (*loc. cit*) however, such hydrocarbons are not attacked, because of the low temperatures employed.

5. *The Estimation of Unsaturated Hydrocarbons by Means of Perbenzoic Acid.*—A few years ago Prileschaef[63] found that ethereal or chloroform solutions of benzoyl peroxide react with hydrocarbons containing double bonds to give addition compounds. These initial products readily decompose to give oxides of the original olefines, which latter are generally very easily hydrolysed to glycols. Prileschaef's experiments were done on hydrocarbons of the terpene series and also on di-isobutylene and decylene. Later, Nametkin and Brussof[64] found that the reaction was quantitative providing that an excess of perbenzoic acid is used for all unsaturated hydrocarbons, whether of straight chain, branched chain or cyclic type[65]. The experimental procedure adopted by

these workers is as follows: The spirit to be tested is mixed with more than twice the theoretical amount of perbenzoic acid in chloroform solution, and the mixture allowed to stand at ordinary temperature for two days, at the end of which time a solution of potassium iodide and sulphuric acid is added and the liberated iodine titrated with thiosulphate. The experimental details are well described and discussed by Nametkin and Abakumovsky[66], and the method has also been described by Levy and Lagrave[67], Zelinsky[68] and Kishner[69]. By this method is obtained the oxygen value (O.V.) of an oil or spirit, corresponding to the iodine value (I.V.) and is defined as the quantity of active oxygen from the perbenzoic acid required for the oxidation of 100 g. of the oil. The ratios

$$\frac{100\ (\text{O.V.})}{16} \quad \& \quad \frac{100\ (\text{I.V.})}{254}$$

then represent the same value, the "unsaturated coefficient," and in most cases the values obtained by the two methods agree satisfactorily.

As a method of quantitative analysis for the unsaturated content of petroleum spirit however, the method has nothing to commend it. Its results are purely empirical, as are iodine numbers also, and, moreover, the method involves a tedious technique.

6. *The Estimation of Unsaturated Hydrocarbons by Kauffman's Method (using Thiocyanogen).*—In the chemical examination of fats and fatty acids Kauffman[70] has used free thiocyanogen for the estimation of unsaturation. The basic reagent used is Rhodan solution, a solution of "free" thiocyanogen $(SCN)_2$ in glacial acetic acid and is prepared by the action of bromine on a solution of lead thiocyanate, thus:—

$$Pb(CNS)_2 + Br_2 = PbBr_2 + (CNS)_2.$$

The free thiocyanogen possesses halogen-like properties and may be regarded as being intermediate between bromine and iodine. From an aqueous solution of potassium iodide it liberates iodine, and this fact is used for its estimation. The Rhodan solution is used exactly as an iodine solution, except of course that it is very unstable, and the figures obtained for unsaturation are called "Rhodan-Iodine" numbers, corresponding with ordinary iodine numbers.

While possessing no obvious advantages over the Hanus or McIlhiney methods for estimating unsaturation, the method possesses many disadvantages, among which may be mentioned the great tendency of the thiocyanogen to polymerise and also decompose when in the presence of water or in sunlight, and even when standing in the dark. The method does not give theoretical results with diolefine or acetylenic substances[71].

7. *Other Methods for the Determination of Unsaturated Hydrocarbons. Aluminium Chloride.*—The condensing and polymerising action of aluminium chloride was used for the removal of unsaturateds by Heusler[72]. As in this reaction new hydrocarbons are formed, the analysis becomes complicated.

Hydrogen Peroxide.—Tausz[40] attempted to use hydrogen peroxide for the selective oxidation of unsaturated hydrocarbons. He used the method of Cross, Bevan and Heiberg[73] in which the hydrocarbon mixture is warmed with 3 per cent. hydrogen peroxide in the presence of ferrous sulphate. He found that amylene, hexene, heptene, cyclohexene and methyl cyclohexene were easily oxidised in a vigorous reaction but that aromatics were also attacked.

Nitric Acid.—Heusler (*loc. cit*) also tried to use this reagent for the purpose of estimating unsaturateds, but was unable to perfect a method. Nitric acid is far too vigorous for the selective removal of olefines, because it also attacks hydrocarbons of other series. For a method based on the oxidising action of nitric acid on olefines, that of Manning[74] described under "The estimation of aromatic hydrocarbons," should be consulted.

Liquid Nitric Oxide.—Smirnov[75] has recently described a somewhat novel method for the estimation of unsaturated hydrocarbons in cracked spirit. The spirit is added drop by drop to liquid nitric oxide kept at $-15°$ to $-20°$ C. and the liquid is then made alkaline and distilled in steam. The distillate, after separation, is dried and filtered through silica gel which is washed with ether. After centrifuging, the ether is removed by distillation. The difference between the volumes of the original and treated gasoline represents the unsaturated content. Opinion on the merits or otherwise of this method should be reserved until more details concerning it are available.

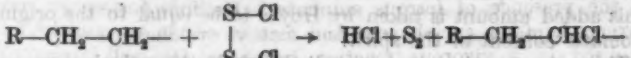
Potassium permanganate.—Unsaturated hydrocarbons are oxidized by permanganate to water soluble compounds such as glycols, acids, aldehydes and ketones[76]. Usually a 5 per cent. potassium permanganate solution is employed. More reactive still than the olefines are the acetylenes; acetylene itself is oxidized by permanganate to oxalic acid.

Heusler[77] attempted to remove the unsaturateds present in brown coal tar by this method. He found, however, that acid potassium permanganate solution removed even less of the unsaturateds than did dilute sulphuric acid (1:3).

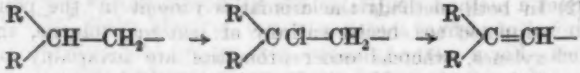
Sulphur monochloride.—Lorand[78] has shewn that sulphur monochloride reacts vigorously with unsaturated hydrocarbons and also

at a moderate rate upon saturated hydrocarbons. Meigs[39] states that the reaction involved is a time reaction in the case of saturated hydrocarbons, since the evolution of hydrochloric acid gas continues for many hours; unsaturateds react quickly and are not responsible for the time element. Based on this, Lorand has suggested a quantitative procedure for the estimation of unsaturateds.

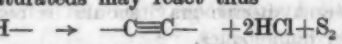
The action of sulphur monochlorides on straight chain paraffin hydrocarbons is a very slow process and probably a chlorination,



with branched chain hydrocarbons the reaction is of the same type and proceeds more rapidly. By prolonged heating the following reaction probably occurs.



and the resulting unsaturateds may react thus



The resulting compounds containing ethylenic and acetylenic linkages easily condense and polymerise. In the method described by Lorand, the oil is dissolved in carbon tetrachloride and refluxed with the sulphur monochloride. After subsequent hydrolysis and washing, the oil is redistilled to its original final boiling point, and either the amount of residue or distillate is suggested as a comparative basis for the degree of unsaturation, since the condensation products formed have much higher boiling points than the original oil.

The Estimation of Aromatic Hydrocarbons.

This may be accomplished by either of the following methods:—

1. By refractive index and specific gravity measurements.
2. By treatment with conc. sulphuric acid.
3. By means of aniline point determinations.
4. By treatment with conc. nitric acid.
5. By means of solvents, and by other methods.

1. *Methods based on density and refractive index measurements.*—Such procedures are founded on the fact that aromatic hydrocarbons possess high specific gravities and high refractive indices. Thole[40] used specific gravities as the basis of his method and the procedure he adopted is as follows:—The spirit under test is divided into three portions, (*a*) 40—95°C., (*b*) 95—122°C. and (*c*) 122—150°C., it

being assumed that these three fractions contain all the benzene, toluene and xylenes respectively. These fractions are separately sulphonated (see later) and the differences in gravities of the fractions before and after sulphonation are used for the calculation of the aromatic content.

Hoyte[81] uses refractive index measurements for the same general purpose. The spirit under test is freed from aromatics by means of sulphuric acid and a 50/50 benzene-toluene mixture added to the residual spirit until its initial refractive index is restored. This added amount is taken by Hoyte to be equal to the original aromatic content of the spirit.

These two methods are now little used, the principal reasons being as follows:—

(1) They are not applicable to routine work, since measurements of specific gravities and refractive indices are long and tedious.

(2) In both methods the aromatics present in the petrol are supposed to consist entirely of benzene, toluene, and the xylenes, whereas other aromatics are invariably present. This fact causes large errors since the higher aromatics have different specific gravities and refractive indices than their lower homologues.

(3) Both methods are seriously affected by the presence of unsaturateds, for the prior removal of which no method of universal application has yet been found. In the presence of unsaturated hydrocarbons any method of analysis based on either refractive indices or specific gravities must lead to erroneous results, due to the formation of alkyl esters, olefine polymers and condensation products.

(4) In the method based on specific gravities, there is no allowance for the fact that the three xylenes have different gravities.

2. *The use of concentrated sulphuric acid.*—The aromatic hydrocarbons are readily attacked by concentrated sulphuric acid to form sulphonic acids. The chemistry of this sulphonation is fully described by Wieland and Sakellarios[82]. The sulphonic acids so formed are soluble in the acid and are eliminated therein, hence a figure for the aromatic content may either be obtained by direct observation of the loss in volume sustained or by calculation from the difference in aniline points before and after treatment. The latter method is the more accurate and by far the more sensitive (see later). In 1916, Kraemer and Bottcher[83] proposed the following method of procedure:—The spirit is shaken with an equal volume of sulphuric acid (containing 80 per cent. by volume of concentrated H_2SO_4 and 20 per cent. by volume of fuming H_2SO_4), in the so called "Kraemer and Bottcher" bottle (see Kattwinkel)[12]. After allowing to stand a short while, the decrease in volume is

measured and this is taken as the aromatic content present originally. Edeleanu and Dulugea[84] found, however, that using this strength of acid with oils rich in aromatics the theoretical absorption was not obtained. They, therefore, worked at an elevated temperature of 50°C., appreciating the fact that at temperatures above 50°C, the saturated hydrocarbons would also be attacked. Krieger[85] found it necessary to use sulphuric acid containing 8 per cent. of excess SO_3 to extract the aromatics from "storm-lamp" benzine and later Pritzker and Jungkung[86] used an acid containing 4 per cent. excess anhydride, and made use of the centrifuge to accelerate the settling out of the oil and acid into two layers after agitation. *Kattwinkel* (loc. cit) has demonstrated that the action of sulphuric acid upon aromatics may be catalysed by the presence of phosphorous pentoxide. By adding this substance to sulphuric acid the latter could be made to remove benzene hydrocarbons even when present in high concentration (*eg.*, 40 per cent.). Riesenfeld and Bandte[87] state, however, in contradiction to the work of those mentioned above that 100 per cent. sulphuric acid is quite sufficient for the complete removal of aromatics from light benzenes when used at a temperature of 40—50 °C. (see also Kattwinkel)[88]. According to Manning[74], 100 per cent. sulphuric acid fails to absorb benzene and toluene completely from light spirits, while fuming sulphuric acid containing 5 per cent. SO_3 effects complete sulphonation but also attacks saturated hydrocarbons. Manning found, however, that 98 per cent. sulphuric acid activated by the addition of 2—3 per cent. of silver sulphate gave theoretical results for aromatic estimations but had absolutely no action upon saturated hydro-carbons.

Ormandy and Craven[89], voice the opinion of most English workers on the subject when they state that 100 per cent. sulphuric acid is the strongest that can possibly be used for this purpose, free SO_3 having a pronounced action upon straight chain and cyclic saturated hydrocarbons. (See also the action of sulphuric acid on naphthenes and paraffins.) The standard English procedure for the estimation of aromatics is as follows[90].

The spirit is shaken with twice its volume of 98 ± 1 per cent. sulphuric acid on a mechanical shaker for 15 minutes. The acid is then drawn off and the procedure repeated for two further periods of 15 minutes each, using in each case the same volume of acid. The aromatic content is calculated from the difference in "Aniline points" of the spirit before and after treatment.

This method for the estimation of aromatics in the absence of unsaturateds seems to be capable of more reliable results than any method yet devised. Little reliable data are available on the solubility of the higher homologues of benzene in sulphuric acid because no systematic work has been done on the subject.

According to Reuter[11] m-xylene is dissolved by sulphuric acid of only 88 per cent. strength, and it is well known that the tetra- and penta-alkyl substituted benzenes react with concentrated sulphuric acid, not only to form sulphonates but also other hydrocarbons. Thus by treating tetramethylbenzene with either cold or warm sulphuric acid, hexamethylbenzene is formed, which cannot be sulphonated. Pentamethylbenzene is converted still more easily into isodurene and octamethyl anthracene[12]. However such reactions are not known to occur with the aromatics boiling within the petrol range and need not concern us here.

3. *The Applications of critical solution temperatures to hydrocarbon analysis.*—It was Chavanne and Simon[93] who first observed that the presence of aromatic hydrocarbons decreased the critical solution temperature of a hydrocarbon mixture in aniline, and, moreover, that the depression of this temperature was directly proportional to the weight of aromatics present. Chavanne and Simon observed that of the four main classes of hydrocarbons, the paraffins have the highest critical solution temperatures and aromatics the lowest, naphthenes and olefines occupying intermediate positions. Accordingly they suggested the determination of critical solution temperatures in aniline for the determination of both aromatics and naphthenes in hydrocarbon mixtures.

It was left to Tizard and Marshall[94] to put the proposed method on a sound experimental basis and in their work they dispensed with the somewhat elaborate and time-consuming critical solution temperature determinations of Chavanne and Simon and substituted for these measurements of "Aniline Points," which may be defined as temperatures at which equal volumes of hydrocarbon mixture and aniline are completely miscible. By this modification the method became applicable to rapid working and did not, as a result, lose any of its accuracy or reliability. Tizard and Marshall found that benzene, toluene and ortho-xylene, in equal proportions by weight, produced identical depressions of aniline point within the limits of experimental error, but that meta and para xylenes lowered aniline points rather less than the same weight of benzene or toluene. As an analytical procedure they proposed that the difference in aniline points of a spirit before and after sulphonation with 98-100 per cent. sulphuric acid should be used as the basis for the determination of aromatic content, the following conversion factors being employed:—

Benzene	1·19
Toluene	1·20
Xylene	1·23

For a spirit containing all three of these aromatics in admixture, the figure 1·2 was suggested to be of sufficient accuracy. It has

been shown by numerous workers (Ormandy and Craven (*loc. cit.*) Brame and Hunter[58], Carpenter[95], Waterman and Perquin[96]) that aniline points are of the greatest utility in the examination of gasoline and kerosine distillates. The method is very sensitive and very accurate results may be obtained by its use provided that certain fundamental factors be remembered. For instance is has been shown by Ormandy and Craven[97] that the presence of water exerts a very definite effect upon aniline points. According to their experiments the presence of 1 per cent. of water raises the aniline point of n-heptane by 6·2° C. and that of cyclohexane 5·6° C. It is therefore essential that all aniline used in these determinations be absolutely dry and quite pure. It is advisable to redistill it immediately before use. It is also usual to standardise the aniline against a hydrocarbon of known purity, and normal heptane seems to be the most convenient hydrocarbon to employ. This substance may readily be obtained 99·9 per cent. pure from Pinus Sabiniana oil. (See Wenzel[98], Thorpe[99], and Brame and Hunter[58].)

The aniline point of pure n-heptane, using water-white pure and dry aniline, is 68° C. (Ormandy and Craven[97]), but because of the fact that aniline is hygroscopic, and is therefore kept absolutely dry only with great difficulty, it is usual to employ for aniline point determinations such aniline that gives an aniline point for normal heptane of 70° C. (Brame and Hunter) (*loc. cit.*).

From the accompanying table (Table IV) of aniline points of pure hydrocarbons it will be observed that :—

(*a*) The aniline points of n-paraffins increase with rise of molecular weight.

(*b*) The aniline points of iso-paraffins are higher than those of the corresponding normal paraffins.

(*c*) The aniline points of naphthenes are lower than those of paraffins, are very irregular, and range from 20°—60° C.

TABLE IV.

Aniline Points of Pure Hydrocarbons (collected data).

Paraffin Hydrocarbons.			
Pentanes.			
n-Pentane	72° C. (*a*)		
2-Methyl butane ..	77° C. (*b*)		
Hexanes.			
n-Hexane	69° C. (*a*)	2·2-Dimethyl butane..	80·75° C.(*b*)
2-Methyl pentane ..	73·8° C. (*a*) 74·7° C. (*b*)	2·3-Dimethyl butane..	72·3° C. (*b*)
3-Methyl pentane ..	69·4° C. (*b*)		

Heptanes.			
n-Heptane	68° C. (*c*)	3-Ethyl pentane	66·3° C. (*d*)
	70° (*d*) & (*a*)	2·2-Dimethyl pentane.	77·7° C. (*d*)
		2·3-Dimethyl pentane.	68·1° C. (*d*) & (*e*)
	71° C. (*e*)	2·4-Dimethyl pentane.	78·8° C. (*d*)
2-Methyl hexane	72·8° C. (*a*) & (*e*)	3·3-Dimethyl pentane.	71·0° C. (*d*)
	74·1° C. (*d*)	2·2·3-Trimethyl butane	72·4° C. (*d*)
3-Methyl hexane	70·5° C. (*d*) & (*e*)		
Octanes.			
n-Octane	72° C. (*a*)	2-Methyl heptane	74° C. (*a*)
n-Nonane	74·50° C. (*e*)		
n-Decane	77·5° C. (*e*)		
n-Undecane	77·78° C. (*f*)		
Naphthene Hydrocarbons.			
Cyclo pentane	18° C. (*a*)	1·2·3-Trimethyl cyclopentane	41° C. (*e*)
Methyl cyclopentane	35° C. (*a*)	Propyl cyclopentane	45° C. (*g*)
1·3-Dimethyl cyclopentane	45° C. (*a*)	Butyl cyclopentane	50·5° C. (*g*)
Ethyl cyclopentane	39° C. (*g*)		
Cyclohexane	31° C. (*a*)		
Methyl cyclohexane	41° C. (*a*)		
1·2-Dimethyl cyclohexane	42·1° C. (*a*)		
1·3-Dimethyl cyclohexane	49·7° C. (*a*)		
1·4-Dimethyl cyclohexane	48·0° C. (*a*)		
1·2·4-Trimethyl cyclohexane	53·6° C. (*a*)		
1-Methyl-4-isopropyl cyclohexane	56·5° C. (*e*)		
Cyclic Hydrocarbons.			
Decahydronaphthalene	34° C. (*e*)	Cyclohexyl cyclohexane	12° C. (*e*)
Tetrahydronaphthalene	20° C. (*e*)	Methyl cyclohexylcyclohexane	15° C. (*e*)
Olefine Hydrocarbons.			
Amylene	14·5° C. (*i*)	Octene	26·5° C. (*e*)
Trimethylethylene	11·0° C. (*j*)	Cetene	68° C. (*e*)
	10·0° C. (*e*)		
Sym. methyl propyl ethylene	18° C. (*e*)	Cyclohexene	−20° C. (*a*)
Hexene	17° C. (*e*)	Isohexene	24° C. (*e*)
Heptene	36° C. (*e*)		

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(*d*) Edgar, Calingaert & Marker, *J. Amer. Chem. Soc.*, 1929, **51**, 1483.
(*e*) Garner, *J. Inst. Petr. Techn.*, 1928, **14**, 713.
(*f*) Carpenter, *J. Inst. Petr. Techn.*, 1926, **12**, 562.
(*g*) Chavanne, *Bull. Acad. roy. Belg.*, 1926, (5), **12**, 105.
(*h*) Chavanne and Becker, *Bull. Soc. chim.*, 1927, **36**, 591.
(*i*) Konowalow, *Ann. Phys.*, 1903, (4), 375.
(*j*) Brame, *J. Inst. Petr. Techn.*, 1927, **13**, 794.

It has already been shown that benzene, toluene and the isomeric xylenes have not identical effects upon aniline points, although the divergencies are not too great, but Tarassof and Azerdaidz[100] have shown that with higher benzene homologues the divergencies are too great to be neglected. They found that the value of the coefficient α in the equation $\rho=\alpha(T-T^1)$ where $\rho=\%$ aromatics, was twice as great for some aromatic hydrocarbons (those occurring in turpentine spirit) as for toluene. Hence for accurate determinations of aromatics by means of aniline points, especially aromatics of high boiling point, it is essential that the value of the constant α be known.

For the determination of naphthene hydrocarbons, Ormandy and Craven[101] and Tizard and Marshall, propose a method based on the aniline point of a spirit after removal of aromatics and unsaturateds.

In this method the following assumptions are made

(*a*) That all paraffin hydrocarbons of whatever type have an aniline point of 70° C.

(*b*) That all naphthenes, whether of five or six-ring structure, boiling up to 95° C. lower the aniline points of paraffins in which they are present at a rate of 0·4° C. per 1%, that for all naphthenes boiling between 95° and 120° C. the figure is 0·3° C, and for all naphthenes of boiling range 120–200° C. the figure is 0·2° C.

(In practice the mean figure of 0·3° C. is used).

Thus if N=% naphthenes and T= aniline point after complete removal of aromatics and unsaturateds by 98·8% acid, the value of N is calculated from the equation

$$N=\frac{70-T}{0{\cdot}3}$$

This method has always been found to give rise to very inaccurate results, and the reasons for this are not difficult to find, for Table IV shows that each of the assumptions upon which the method is based is quite unfounded.

Garner[102], in a method only recently described, has appreciated the fact that paraffins and also naphthenes have aniline points depending upon their boiling points. He characterises the spirit to be tested by its mid-point, and uses a chart, which is reproduced in Fig. 1 for the calculation of naphthene and paraffin concentrations. Using such a modification of procedure the method gives more reliable results, but nevertheless these can only be approximate.

It will be noticed that all the foregoing methods of analysis using aniline points depend, for their accuracy, upon the efficiency of

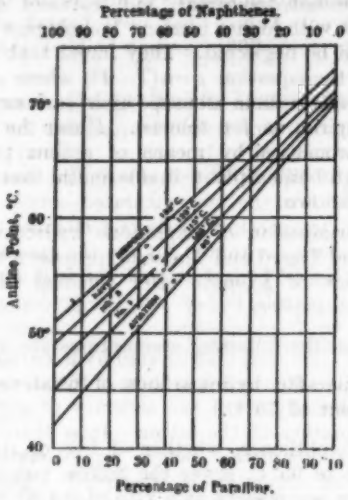

FIG. 1.

sulphuric acid in effecting the quantitative removal of unsaturateds and aromatics. Obviously in the determination of aromatics, if these are not completely removed, the figure obtained from the aniline points will be too low, and, moreover, will result in the naphthene figure being far too high. To overcome this difficulty, Aubrée[163] has developed a method for estimating aromatics based upon critical solution temperatures in which the removal of these hydrocarbons by chemical means is rendered unnecessary.

If T=C.S.T. of original spirit
T^1=C.S.T. of spirit after removal of aromatics
$\theta\eta$=C.S.T. of naphthenes
& $\theta\rho$=C.S.T. of paraffins
A= % aromatics, N=% naphthenes &
P=% paraffins.

Then $$A=K(T^1-T)$$

and $$N=\frac{\theta\rho-T^1(100-A)}{\theta\rho-\theta\eta}$$

or $$\frac{N(\theta\rho-\theta\eta)}{100-A}=\theta\rho-\left(\frac{A}{K}+T\right)$$

in which T^1 does not occur.

If a second solvent is now used, therefore, and the corresponding values for K^1, $\theta^1\rho$ and $\theta^1\eta$ obtained in a second equation, from the two equations the two unknowns A and N can be calculated. As the second solvent Aubrée has used benzyl alcohol, of which the high boiling point, 206°, (aniline boils at 183°C) is favourable to its utilisation.

Aromatics are soluble in all proportions in benzyl alcohol, as well as in aniline, at ordinary temperatures, and the fact that critical solution temperatures of hydrocarbons in benzyl alcohol are lower than in aniline is especially valuable in the examination of very volatile spirits. For the two saturated series, the variation in critical solution temperature from one member to another of the same series is more accentuated than in the case of aniline, and this fact makes the use of benzyl alcohol not well adapted to approximate analyses of petrols, but only to the precise analysis of narrow cuts separated by fractionation.

In view of the fact that unsaturated hydrocarbons also have very low aniline points, often as low as those of the aromatics, the presence of this will materially affect the accuracy of any results obtained in the determination of the latter. It is therefore necessary to remove olefines completely before an estimation by means of aniline points, of aromatics is attempted. According to Garner (*loc. cit.*), a given weight of unsaturateds will depress the aniline point of a hydrocarbon mixture to $\frac{2}{5}$ the extent of that caused by the same weight of aromatics.

Erskine[104] has described a method for the determination of aromatics in which he determines critical solution temperatures in nitro benzene instead of in aniline. In this case the miscibility temperatures are much lower, as is shown in Table V, and it is interesting to note that these temperatures decrease with rise in molecular weight of the hydrocarbon, whereas with aniline they increase.

TABLE V.

Critical Solution Temperatures of Hydrocarbons in Nitro-Benzene.

n-Pentane	24·5°
iso-Pentane	31·25°
n-Hexane	14·8°
iso-Hexane	24·05°
n-Heptane	11·5°
iso-Heptane	18·05°

Erskine claims that the method using nitrobenzene gives greater accuracy than that using aniline, because (*a*) a given percentage of

aromatics gives a greater depression of C.S.T., and (*b*) the lower temperatures that may be employed prevent evaporation losses.

5. The Estimation of Aromatic Hydrocarbons by methods involving the Use of Nitric Acid or Nitro-Sulphuric Acid.—The benzene hydrocarbons are readily nitrated, and this fact has been used as the basis for the quantitative estimation of aromatics in methods described by Hess[105], Egloff and Morrell[13], Garner [108], and by Manning[74].

According to the method of Hess, the aromatics are converted into their mononitroderivatives, and these are extracted from the unchanged hydrocarbons by means of concentrated sulphuric acid in which only the nitro-derivatives are soluble.

The method used by Egloff and Morrell is unique in that nitro-sulphuric acid is used of such a strength that nitro-aromatic bodies are not soluble therein, but separate out as a distinct layer. The volume of this layer is multiplied by the factor 4·3 to convert it into percentage aromatics.

Riesenfeld and Bandte[106] have tested these two nitration methods. The Hess method gave good results with both high and low aromatic contents, but the Egloff and Morrell method gave values too low for low aromatic contents and values too high for high aromatic contents. Garner makes use of fuming nitric acid at low temperatures,—10° to –15° C. According to this method, the petrol to be tested (from which it is not necessary to remove unsaturateds in this case) is shaken with fuming acid at the temperature mentioned, and the nitro bodies which dissolve in the residual petrol are washed out by means of more fuming nitric acid. From the difference in aniline points of the petrol before and after such treatment is obtained the "aromatic hydrocarbon equivalent"—*i.e.*, aromatics and olefines calculated as aromatics on the aniline point basis. From this figure is obtained the aromatic hydrocarbon content by subtracting from it the olefine content arrived at by other means, assuming that unsaturateds depress aniline points to 2/5 of the extent due to aromatics.

Then if A = % Aromatics, B = % olefines, and a = aromatic equivalent.

$$A + 2/5\,B = a$$

and $A + B = b$ = total loss to nitric acid

or $B = 5/3\,(b - a)$ and $A = b - B$.

The method described by Manning (*loc. cit.*) makes use of a nitrating mixture of 10 per cent. concentrated nitric acid in sulphuric acid, but the experimental procedure is somewhat novel.

A small sample of the oil to be tested is weighed in a small U-tube and vaporised by drawing through it a current of CO_2—free air or nitrogen.

The oil vapours are absorbed in the nitration mixture contained in small "potash-bulbs." The increase in the weight of the bulbs corresponds to the aromatic unsaturated content of the oil, after a small correction has been applied for the retention of saturated vapours. The nitration of the aromatics is completed by adding a little more nitric acid and heating for 2—3 hours. The unsaturated hydrocarbons are at the same time oxidised to carbon dioxide, acids and other compounds soluble in water or aqueous alkali solution. The nitrated aromatics are extracted and weighed, and from the weight obtained the aromatic percentage is calculated.

Up to the present, no results of work done using this method have been published other than those given by Manning himself, so that opinions on the merits of the method are reserved. It would appear, however, that under the experimental conditions some olefinic bodies might be converted into polynitro bodies and weighed as such instead of being converted to water-soluble compounds.

5. *The use of Preferential Solvents in the Determination of Aromatics.*—The most widely used solvent for the extraction of aromatics from petroleum distillates is sulphur dioxide, originally suggested by Edeleanu.[106] It is used commercially for the extraction of aromatic hydrocarbons from kerosenes and illuminating oils. This solvent has been the subject of laboratory tests by Egloff, Morrell and Moore,[107] who shew that sulphur dioxide also dissolves unsaturateds. This solvent has not yet been employed for the quantitative determination of aromatic hydrocarbons. Another well-known solvent for aromatic hydrocarbons is dimethyl sulphate, originally proposed by Valenta,[108] who claims that it has no solvent action upon paraffins or naphthenes. This claim is refuted by Graefe[109] and by Harrison and Perkin.[110]

Graefe conducted very complete tests and came to the conclusion that dimethyl sulphate, although admittedly dissolving aromatic hydrocarbons also possessed a very definite solution action on saturated hydrocarbons. Moreover, he found that the solubility of an oil in dimethyl sulphate was proportional to the amount of this solvent used.

Harrison and Perkin came to the same conclusions and proved that dimethyl sulphate cannot be used in quantitative determinations.

Taylor[111] has suggested the use of diethyl sulphate for the same purpose, because it is non-poisonous, whereas dimethyl sulphate is excessively poisonous. In the examination of synthetic mixtures however, he found that the substance also gave misleading results.

He tested the two solvents, side by side, on synthetic mixtures of highly refined petroleum oil and benzene with the results given in Table VI.

TABLE VI.

Taylor's Results on the Solubility of Saturated Oils in Dimethyl and Diethyl-sulphates.

Petroleum oil present. %	Dimethyl sulphate residue. %	Error. %	Diethyl sulphate residue. %	Error. %
0·0	0·0	0·0	0·0	0·0
10·0	8·5	15·0	0·0	—
20·0	22·3	11·5	8·0	60·0
30·0	35·0	16·7	23·0	23·3
40·0	46·7	16·8	36·2	9·5
50·0	57·5	15·0	48·3	3·4
60·0	67·1	11·8	60·4	0·7
70·0	76·1	8·7	70·2	0·3
80·0	84·9	6·6	80·9	1·6
90·0	92·9	3·2	90·5	0·6
100·0	100·0	0·0	100·0	0·0

In each of the above experiments the relative amounts of oil and alkyl sulphate used were 5 and 8 respectively by volume.

It is thus evident that diethyl sulphate, though better than its dimethyl homologue for low aromatic concentrations, is quite unsuitable for quantitative estimations.

Riesenfeld and Bandte[112] have also pointed out that dimethyl sulphate gives results for aromatic contents which are too high.

After a survey of the solvents used for estimating aromatics, Gohre[113] discusses several new solvents that he investigated, including four which he claims to give accurate results. According to Gohre, lævulic acid gives theoretical results for the aromatic contents of oils containing up to 90 per cent. of these constituents. Phenylhydrazine he found suitable for oils of high boiling point, and glycol monoacetate suitable for light oils, except when the aromatic content is high, when the mixture must be cooled in ice. Furfuraldehyde was also found to be suitable if used at —10° C.

Kattwinkel[114] has recommended the use of sulphoacetic acid mixed with acetic anhydride, which is capable of dissolving benzene hydrocarbons from light oils under special conditions.

Analytic methods based on preferential solubilities are, however, not to be recommended. They are based on unsound principles and give erroneous results.

The use of Formaldehyde and Methylal for the Estimation of Aromatic Hydrocarbons.—When formaldehyde in the presence of concentrated sulphuric acid is added to a mineral oil, the unsaturated and aro-

matic bodies are precipitated as a yellow solid. The "formolite number" of an oil is the number of grams of dried solid so produced from 100 c.c. of the oil. The solid is called formolite. The paraffins and naphthenes do not react.

This reaction was first suggested for the quantitative removal of aromatics from benzenes by Nastjukoff,[115] but as olefines and cyclic unsaturated hydrocarbons are also attacked these must be previously removed. The difficulties attending this operation have been described.

Later, Severin,[116] used this method for the quantitative estimation of benzene, toluene and xylene.

Heer[117] found that the use of methylal, instead of formaldehyde, was advantageous, because it acts as solvent as well as a condensing agent, and is more sensitive than formaldehyde. It can detect 0·05 per cent. of benzene.

This method appears now to be no longer used.

The Estimation of Naphthene and Paraffin Hydrocarbons.

After unsaturated and aromatic hydrocarbons have been estimated and removed, there remains a mixture of naphthenes and paraffins. The determination of these two classes of hydrocarbons when present together is an exceedingly difficult task, and up till the present no satisfactory method has yet been discovered.

The only method which gives even approximately accurate results is that described by Tizard and Marshall[94] and Ormandy and Craven,[101] and which has already been mentioned. This method, although the only one available, must only be used with caution, and it must be remembered that the figures it gives are only approximate. If the method is used in accordance with the recommendations of Garner,[102] then more reliable results are obtained.

Other methods of analysis which are being proposed are, however, worthy of notice.

Danaila, Andrei and Melinescu (*loc. cit.*) have proposed that the cyclohexane series of naphthenes be estimated by dehydrogenating them by passage over a nickel catalyst at a suitable temperature. In this way they are converted into benzene hydrocarbons, and may be estimated as such by means of 98·8 per cent. sulphuric acid in the manner already described. Obviously, cyclopentane derivatives cannot be estimated in this way.

A method for separating naphthenes and paraffins depending on differential solubility in liquid sulphur dioxide has been favourably reported on by Egloff, Morrell and Moore,[107] but it seems extremely unlikely that these separations would be clean cut. The solubilities underlying the method have been examined and reported by Seyer[118] to be unfavourable.

Tausz[119] has observed that certain bacteria eg. B. aliphaticum and B. aliphaticum liquefaciens, will consume paraffin hydrocarbons, but are entirely without action on naphthenes. Hessel[120] states that the reactions involved are oxidations.

Oxidation of the naphthenes by a current of air in the presence of alkali, at a temperature which will not permit attack of paraffin hydrocarbons has been suggested by Charitschkoff.[121] The oxidation may be with dry air at 150° C. in the presence of 1 per cent. of powdered caustic potash as a catalyst. The naphthenic acids so produced may be recognised by the green colour which the copper salts impart to a benzene solution. Under the conditions of oxidation, however, paraffins are probably also attacked.

The combination of the naphthenes with benzoyl chloride in the presence of anhydrous aluminium chloride, leaving the paraffins unattacked, has been suggested by Marcusson.[122] Young [123] has used chlorsulphonic acid to produce from mixtures of naphthenes and paraffins pure normal paraffins. According to Aschan[124] paraffins with branched chains react even at ordinary temperatures with this acid, di-isopropyl and isopentane dissolving completely with a brisk evolution of hydrochloric acid gas. Nitric acid acts upon both paraffin and naphthene hydrocarbons, prolonged treatment with concentrated acid causes oxidation, while moderating the reaction causes the formation of nitro compounds. The nitration occurs the more readily the greater the size of the hydrocarbon molecule, and strong nitric acid, it seems, is also capable of splitting and nitrating the molecules of secondary and tertiary paraffins at the same time (Beilstein and Kurbatow).[125] The normal and quarternary paraffins are scarcely attacked at ordinary temperatures by concentrated or even by fuming nitric acid; the secondary and tertiary hydrocarbons, on the contrary, react easily with auto heating and the formation of carbon dioxide, lower carboxylic acids and tertiary nitro derivatives.[126]

Fuming nitric acid is reported to attack some naphthenes at ordinary temperature, and with concentrated acid, the naphthenes with branched chains are the more easily attacked.

Heusler[127] removed naphthenes from a crude nonane cut by dropping the latter into four times its volume of fuming nitric acid. This method of freeing paraffins of naphthenes has been recommended by Ubbelohde.[128] Such a generalisation is probably not supported by fact, but in any case it is true that naphthenes react with nitric acid more readily than do the paraffins, and of the naphthenes, the cyclopentanes are more easily attacked than the cyclohexane hydrocarbons.

In their action towards sulphuric acid, the naphthenes and paraffins are also very similar. The gaseous alicyclic hydrocarbons

are easily attacked by concentrated sulphuric acid; for example, cyclopropane and methyl cyclopropane are completely absorbed. 1·1 dimethyl cyclopropane is even soluble in dilute sulphuric acid (2:1). Warm fuming sulphuric acid attacks naphthenes containing tertiary carbon atoms more strongly than it attacks paraffins, but branched-chain paraffins are also attacked to a marked degree.[16] According to Sentke[17] normal octane is also affected by concentrated sulphuric acid at ordinary temperatures, but this statement needs confirmation.

It will thus be seen that neither nitric acid nor sulphuric acid is a suitable reagent to employ for the separation of naphthene and paraffin hydrocarbons, for although in general the naphthenes are the more reactive, part of the paraffin content might also be destroyed, or part of the naphthenes unattacked, perhaps both, depending upon the severity of the treatment.

Conclusion.

From the foregoing account of hydrocarbon oil analysis, as applied particularly to motor spirits, it will be appreciated that little purpose is served in conducting experimental work, upon which analytical methods are to be based, on hydrocarbon mixtures of unknown composition. Only by working in terms of pure hydrocarbons can a reliable method be obtained, and such substances should include hydrocarbons of all classes and types. Such work, though necessarily long and tedious, would prove of tremendous value, and should be aimed at settling once and for all time the many points which are the subject of so much controversy.

Department of Oil Engineering and Refining,
The University of Birmingham.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

RUMANIAN BRANCH.

Oil Well Pumping in Rumania.

By J. J. Honegger.

A meeting of the Rumanian Branch of the Institution of Petroleum Technologists was held at Ploesti on September 27, 1929, when a paper was read by Mr. J. J. Honegger on "Oil Well Pumping in Rumania." During the last few years deep well pumps have been employed to replace bailing when productions have fallen to a figure which renders swabbing and bailing unprofitable. The author prefaced his remarks by emphasizing the fact that pumping introduced a host of problems calling for highly skilled attention to obtain success, due to the sand in suspension, the presence of water and emulsions and variations in the viscosity and character of the oils. Not only each field, but each sand and even each well presented some problems of complexity.

A brief description was given of the various types of pump barrels and plungers in general use to meet different conditions and particular mention was made of the circulating type wherein the oil is forced upwards in small central tubing, which constitutes the sucker rods, and clean fluid can be pumped from the surface to mix with the dirty fluid raised. The higher velocity in the smaller tubes assists in carrying sand to the surface.

The difficulty of finding a suitable steel for sucker rods in deep wells was referred to by Mr. Honegger and the general need for gas anchors was also stressed. Mention was made of a well swabbing initially 15 tons of oil per day from strata of Dacic age where the decline rate was 9½ per cent. per month, whereas on the pump the output rose to 20 and even 30 tons a day with a decline rate of 4 per cent. per month. The gas-oil ratio was, it is claimed, reduced by 20 per cent.

During the subsequent discussion Mr. H. F. Crooks asked questions about paraffin troubles in pumps and it transpired that the pumps waxed up in about one month on the Ceptura field. A remedy had been effected by admitting steam to the casing head. Mr. Dailey asked if collar wear had been observed on sucker rods and in reply

it was stated that such wear had been noticed and overcome by fixing bronze rings to the couplings with a clearance of 5 mm. Mr. E. C. Masterson said gas and not sand was the main trouble at Chicuira, and incidentally mentioned that a well 620 metres deep pumped with 2-inch tubing and ¾-inch sucker rods was producing 25 tons daily with a power consumption of 165 kw. a day, where previous bailing took about double the power for 20 per cent. less production. This speaker referred to the value of counter-balancing. The author referred to a 200 metre well in which a plain cold drawn steel barrel pump raised 3 tons daily for six months to a year without pulling and intimated that this was an exceptional occurrence in Rumania.

A. BEEBY THOMPSON.

BOOKS RECEIVED.

THERMAL PROPERTIES OF PETROLEUM PRODUCTS. C. S. Cragoe. U.S, Bureau of Standards, Misc. Publ. No. 97. Supt. of Documents. Washington, D.C. 15 cents.

Numerous tables in forms convenient for use in engineering give the various thermal properties of petroleum products and embody the results of a critical study of the data available in literature, together with unpublished data obtained by the Bureau of Standards. The tables contain the most reliable data available, and the experimental basis and the agreement of the tabulated values with experimental results are given. Each table has a statement regarding the estimated accuracy of the data and an example of the use of the data.